



# OUTLINES OF GENERAL CHEMISTRY





## PART II

## CHEMICAL LAWS OF ENERGY

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OUTLINE~~S~~  
OF  
GENERAL CHEMISTRY

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**G. D. ROPE.**

## AUTHOR'S PREFACE

THIS book has been written mainly to supply a want felt in my own teaching experience. It is designed to meet the requirements of the student who, while not intending to devote himself to the detailed study of General Chemistry, still wishes to follow intelligently the progress recently made in this important branch of science. Numerous assurances of my colleagues have convinced me that there is an actual demand for such a work.

In conformity with this design, I have abstained as far as possible from the use of mathematical formulæ, and have always striven after clearness of exposition. The task has been all the more difficult that the course of study still pursued by the average chemist has laid upon me the necessity of avoiding the employment of higher mathematics. When possible, I have applied graphic methods: when a clear proof could not be given in an elementary way, I have contented myself with simply stating the result. Of course one can with the help of more or less cumbrous mathematical apparatus give an "elementary" proof of almost anything; but experience has shown that such diffuse page-long calculations are of no real aid to the comprehension of the subject. Another reason that has led me to adopt the above mode of treatment is that the reader who has only an acquaintance with elementary mathematics may be brought to see the necessity of acquiring at least the rudiments of the higher analysis. Without such knowledge it is possible (as I have endeavoured to show in the following pages) to understand both the methods and the results of General Chemistry; but for successful work in this field such knowledge is indispensable.

Within the last three or four years an enormous advance has been made in chemistry by the theories of solution and of electrolytic dissociation, due respectively to van 't Hoff and Arrhenius. I hope not only to have rendered a service to students by the elementary exposition of these epoch-making theories and the experiments on which they are based, but also to have contributed towards their general recognition amongst my fellow-teachers—a recognition which can scarce be longer delayed.

In accordance with the general character of the work, I have given as references only the authors' names and the year of publication, which if need be will suffice to identify the original memoirs in the indexes and catalogues of papers now everywhere accessible.

W. OSTWALD.

LEIPZIG, *July* 1889.

## TRANSLATOR'S PREFACE

To what Prof. Ostwald has said with regard to the scope and object of the present work the Translator has nothing to add. He can only hope that the publication of the book in English form will conduce to the acceptance in this country of the new ideas to which the author has alluded. The singular disregard of the discoveries of van 't Hoff and Arrhenius amongst the English-speaking scientific public must be in great measure attributed to the want of a connected account of them from one uniform point of view,—a want which this volume amply supplies.

The student who wishes to pursue his study of the subject further will find plentiful details in the author's *Lehrbuch der allgemeinen Chemie* (2 vols. Leipzig, Engelmann), a second edition of which is in preparation.

With regard to the English version, its substantial accuracy may be guaranteed from the fact that the revised proofs have all passed through the author's hands. The Translator has also to thank Dr. Alex. Smith and Mr. T. S. Murray for kind assistance in proof-correction.





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# PART I

## CHEMICAL LAWS OF MASS



# BOOK I

## MASS

### CHAPTER I

#### FUNDAMENTAL LAWS

CHEMISTRY is the science which treats of the different forms of matter, their properties, and the changes which they undergo. We can only know and distinguish between the objects of the external world by means of their properties, *i.e.* by the direct or indirect impressions they make on our organs of sense. These objects we call substances when we consider them with reference to properties which are independent of their quantity and of their position in time and space.

It may be frequently noticed that one substance changes into another, *e.g.* wood into charcoal, wine into vinegar, so that instead of the original substance we get another with quite different properties. Such changes are chemical processes, and are subject to definite laws, an exact knowledge of which has only been obtained in the last hundred years, though centuries of patient work had been occupied in paving the way to them. The most general of these laws is that which is usually called the law of the Conservation of Matter. It may be stated as follows—

The total mass of the substances taking part in any chemical process remains constant.

But we know that the masses of all bodies are at any one place proportional to their weights; we may consequently substitute weight for mass in the above law.

Nowadays that we are accustomed to look upon ponderable matter as something objectively existent, such a law appears to us as self-evident. This habit of thought, however, is not more than a hundred years old, for before the end of the eighteenth century (when Lavoisier first expressly stated the law) it was quite as customary to assume the contrary as not.

The law may be proved experimentally by instituting any kind of chemical process within a completely closed space, *e.g.* in a sealed glass vessel; the weight of the vessel and its contents after the operation remains absolutely the same as at first. On a gigantic scale the same proof is furnished by the solar system. The velocity of revolution of the planets round the sun is dependent on their masses; since now the length of the year has not changed appreciably from the remotest historical times, we must come to the conclusion that, in spite of the manifold chemical changes which take place on the earth and in the sun, the masses of these bodies have remained unaltered.

We might now perhaps be inclined to conceive a chemical process in the following manner: substances consist of indifferent matter, which during any chemical process simply becomes invested with different properties from those which it originally possessed, without, however, itself undergoing any real alteration.

This conception was as a matter of fact for a long time prevalent, but the following laws, empirically discovered, are in discordance with it—

If one substance is transformed into another, then the masses of these two substances always bear a fixed ratio to each other.

Thus 100 parts of zinc on combustion yield exactly 124.5 parts of a white powder (zinc oxide), no matter how much zinc is taken or how the combustion is conducted. Zinc oxide may also be obtained by methods widely differing from ordinary combustion; but in all cases its properties are the same, and a given quantity of zinc always yields the proportionate quantity of oxide.

Such a transformation of one substance into another of different mass can only take place according to the first law when a second substance participates in the reaction.

The following law, therefore, is in intimate connection with that given above—

If several substances react together, then their masses, as well as those of the new bodies formed, always bear fixed proportions to each other.

It is here particularly to be noticed that the changes in the properties of substances always take place by leaps and bounds in chemical reactions. If we subject zinc to combustion, we never find any intermediate stages between it and its oxide, such as might occur if the whole mass of zinc gradually altered its properties until it acquired those of zinc oxide; but that the zinc changes directly into oxide part by part. If the operation is interrupted, that part of the zinc which has undergone any change is found to be completely converted into oxide, while the part which has not reached this

stage is unchanged zinc. We must conclude from this that for the existence of a substance the presence in perfectly definite proportions of the particles of which it is composed is necessary. The cause of these laws cannot be comprehended on the assumption of the indifference of matter, so that this view has been abandoned and the following one substituted for it.

Substances consist of very small particles of different kinds, which only alter their arrangement and not their nature during any chemical process. The mass, therefore, suffers no change. Different substances contain these dissimilar particles in different proportions, in such a way that each substance consists of one or more definite kinds of them in definite proportions. From this assumption the above laws follow of necessity.

Such "hypotheses" as the above have not the same claim to truth as the abstract laws themselves, but their employment has its origin in the organisation of the human mind, which handles abstract truths much less easily by themselves than with the help of an illustrative image. The value of a hypothesis depends on the one hand on the convenience, and on the other on the comprehensiveness of the image, and the extent to which a hypothesis possesses these properties is decisive as to whether it ought to be retained or not. Thus it continually occurs in the history of science that such a hypothesis, which had served to represent a certain number of laws satisfactorily, has had to be given up because new laws were discovered of which it could not take account, so that another had to be found to take its place. It is customary in such a case to say that the older hypothesis has been refuted; but this is not quite correct. A hypothesis can neither be proved nor disproved. It is merely a tool which is rejected when found to be no longer serviceable.

The hypothesis stated above concerning the nature of substances and of chemical processes is so far serviceable as to give us a clear idea of the laws we have mentioned; not only, however, does it do this, but it presents to us the possibility of foreseeing other regularities, and consequently advances scientific investigation from the stage of blind groping to that of conscious progress.

When the transformation of substances into others is accompanied by change of mass, then by the first law this can only take place either by several substances uniting to form one, by one substance decomposing into several, or by both of these processes together. The substances into which a given body decomposes (so that the sum of their masses is equal to that of the original substance) are called its component parts, or simply components. If these components are in their turn subjected to decomposing influences they may often be split up, and so the process may be carried on; at last, however, we come to substances which resist all attempts at their further decomposition.

In the sense of the above hypothesis, such undecomposable



substances or elements must be looked on as the ultimate components of existing substances, *i.e.* the latter must be composed of particles of these elements. In accordance with this view, we find that we can by proper methods regain the elements from compounds which they formed by their union.

We might ask, "Is matter infinitely divisible?" Since the Infinite in any form cannot be the subject of experience, this question is evidently an objectless one for chemistry, which is essentially an experimental science. If we wish, however, to make further use of the above hypothesis, we must obviously assume that matter is not infinitely divisible, for on this assumption only has the hypothesis that the elements exist as such in chemical compounds any meaning: the question whether further divisibility is conceivable need not be touched upon. This assumption is supported by a remarkable law discovered by Dalton in 1808.

If a substance A unites with another B in several proportions, then the masses of B which unite with one and the same mass of A always stand in simple ratios to each other. Thus, for example, oxygen and nitrogen, the components of atmospheric air, unite to form several compounds, which contain to 100 parts of nitrogen 57.1, 114.3, 171.4, 228.6, and 285.7 parts of oxygen respectively. These numbers are to each other as 1 : 2 : 3 : 4 : 5.

Our hypothesis explains this fact as follows. If we admit that matter is composed of small particles, we must inquire if these particles—which shall be called once for all atoms—are in a given substance all similar, or if they may differ from each other, like grains of sand. If we make the latter assumption, we ought to be able to get two specimens of water with somewhat different properties, just as we can separate sand into fine and coarse particles. Experience at first sight seems to speak in favour of this, for river-water, spring-water, and sea-water are all different. A more minute investigation, however, shows the contrary. These varieties of water differ from each other only because they are not pure, *i.e.* are not water alone. If we by proper means free them from all foreign bodies, we obtain specimens of water which agree with each other in every respect—so completely that the most exact measurements can detect no difference in their properties.

We must therefore assume that the atoms of every pure substance are all like among themselves. Then Dalton's law of Multiple Proportions follows of necessity. For a compound of A and B in varying proportions can only be formed by one, two, three, etc. atoms of A uniting with one, two, three, etc. of B, so that only rational proportions can obtain between the atoms of A and B, and therefore the quantities of B which can unite with a given quantity of A must stand to each other in simple ratios.

From this result the atomic hypothesis leads us to a further

conclusion. If the above conception of atoms be in accordance with the facts, then all relations of mass in chemical compounds must be regulated by the masses of the several atoms. Without having to enter upon the determination of the absolute masses of the atoms, we must require that the relations of the masses of all combinations of the elements shall be expressible by certain numbers (or their multiples), which are definitely fixed for each element and which represent the relative masses of the different atoms.

Hydrogen combines with oxygen for example in the proportion 1 : 8, with sulphur in the proportion 1 : 16. We therefore require that all compounds of oxygen with sulphur shall be expressible by the numbers  $m8 : n16$ , where  $m$  and  $n$  are whole numbers. As a matter of fact, we know compounds of these elements in which their masses are represented in the proportions  $2 \times 8 : 16$  and  $3 \times 8 : 16$ , and no others.

Dalton drew these conclusions at once when his discovery of the law of Multiple Proportions led him to the atomic hypothesis and found them confirmed by experiment.

The number and nature of the experiments were, however, insufficient to place a proposition of such importance on a firm footing. Berzelius was the investigator who accomplished this task. The result at which he and all his successors arrived was ever the same; they found that the requirements of the atomic theory are always strictly fulfilled.

Such a broad and far-reaching agreement of the empirically determined abstract laws with the atomic hypothesis formed to explain the cause of these laws justifies us in expecting still further concordance between this hypothesis and experience. In fact, all our chemical experience harmonises with the atomic theory and finds in it an easy mode of expression, so that in what follows we shall always employ it. But once for all be it understood that the atomic hypothesis is only a mode of picturing to ourselves what we know of the behaviour of substances. What the "real" nature of matter is, is to us a matter of complete ignorance, as it is of complete indifference.

To conclude this chapter, we may again give a short statement of the theory of chemical compounds in the light of the atomic hypothesis.

All substances consist of discrete particles of finite but very small size—of atoms. Undecomposable substances or elements contain atoms of the same nature, form, and mass. If chemical combination takes place between several elements, the atoms of these so arrange themselves that a definite and usually small number of atoms of the combining elements form a compound atom which we call a molecule. Every molecule of a definite chemical compound (chemical species)

contains the same number of elementary atoms arranged in the same way.

If the same elements can unite to form different compounds, the elementary atoms composing the molecules of the latter are either present in different numbers, or if their number be the same, they are differently arranged.

## CHAPTER II

### THE ELEMENTS

THE only way of learning whether a given substance is simple or compound is to assume that it is compound and apply all known methods to effect its decomposition.

If the products we obtain always weigh more than the substance itself and never less, no matter to what changes it has been subjected, then, provided each change is complete and accompanied by no loss of substance through our imperfect methods, we are constrained to regard that substance as an element.

The conception of an element in the chemical sense is therefore that of an undecomposed, not of an undecomposable substance, and is consequently liable to some extent to change, being specially dependent on the resources of chemical analysis, so that it must remain quite uncertain whether or not the substances called elements have any real title to the simplicity implied in the name. At any rate, we cannot decide whether our present "elements" are actually undecomposable or not. But one thing we can decide, viz. if they are substances of the same or of different orders. The facts almost without exception go to show that if the elements are really composite they must at least be composite to the same degree, so that the successful decomposition of one of the present elements, say copper, would make it almost certain that the other elements could be decomposed in the same way. The reasons for this conclusion can only be given later, when the properties of the elements and their numerical relations have been discussed.

The number of elements hitherto discovered is about seventy; an exact figure cannot be given, as the record of some substances usually looked on as elements is not yet closed and their claims are therefore doubtful. The following is a list of the undoubted elements—

Aluminium, Al.	Barium, Ba.	Boron, B.	Cæsium, Cs.
Antimony, Sb.	Beryllium, Be.	Bromine, Br.	Calcium, Ca.
Arsenic, As.	Bismuth, Bi.	Cadmium, Cd.	Carbon, C.

Cerium, Ce.	Iron, Fe.	Phosphorus, P.	Tantalum, Ta.
Chlorine, Cl.	Lanthanum, La.	Platinum, Pt.	Tellurium, Te.
Chromium, Cr.	Lead, Pb.	Potassium, K.	Thallium, Tl.
Cobalt, Co.	Lithium, Li.	Rhodium, Rh.	Thorium, Th.
Copper, Cu.	Magnesium, Mg.	Rubidium, Rb.	Tin, Sn.
Erbium, Er.	Manganese, Mn.	Ruthenium, Ru.	Titanium, Ti.
Fluorine, F.	Mercury, Hg.	Samarium, Sm.	Tungsten, W.
Gallium, Ga.	Molybdenum, Mo.	Scandium, Sc.	Uranium, U.
Germanium, Ge.	Nickel, Ni.	Selenium, Se.	Vanadium, V.
Gold, Au.	Niobium, Nb.	Silicon, Si.	Ytterbium, Yb.
Hydrogen, H.	Nitrogen, N.	Silver, Ag.	Yttrium, Y.
Indium, In.	Osmium, Os.	Sodium, Na.	Zinc, Zn.
Iodine, I.	Oxygen, O.	Strontium, Sr.	Zirconium, Zr.
Iridium, Ir.	Palladium, Pd.	Sulphur, S.	

It is presumed that the reader, from his knowledge of descriptive chemistry, is already sufficiently acquainted with the nature and properties of the chemical elements, so that these may be passed over here. Attention need only be drawn to one point, viz. that by far the greater number of the elements are metals, the similarity of whose properties forms one of the arguments which speak in favour of the assumption that the elements are substances of the same order.

To the names of the elements in the above table are affixed their abbreviated symbols. Such symbolic representations have been in vogue in chemistry from the earliest times, when in particular the metals obtained the signs of the planets. They had at first only a qualitative significance, and stood simply for the name of the substance. With the development of the atomic theory, however, they received an extended, quantitative, meaning, as they then had to represent an atom of the substance in question. Dalton, immediately after propounding the atomic hypothesis, elaborated such a system of symbols, which, however, consisted of arbitrary signs, and consequently made great demands on the memory. Berzelius was the first to invent a really practical symbolic notation, namely, that in which the first one or two letters of the names of the elements were used to represent their atoms.

Chemical compounds are symbolised by writing the elementary symbols alongside each other. If several atoms of an element are present in the compound, its symbol is in general not repeated, but has merely the number of the atoms affixed to it, commonly in the place of the mathematical index, more unusually prefixed as a factor. In complex formulæ a great saving of space is thus effected.

The significance of chemical formulæ is not exhausted by the indication of the nature and number of the atoms. In the first place, as a knowledge of the relative atomic weights is postulated, they give us complete information regarding the relative masses of the elements

in the compound. Again, it is sought through them to give a representation of the more or less intimate relations in which the atoms stand to each other in the molecule. With this intention we write constitutional formulæ, in which these relations are exhibited by the relative positions of the symbols.

## CHAPTER III

### ATOMIC WEIGHTS

ACCORDING to the preceding chapter there exists for each element a definite number, which either by itself or when multiplied by a whole number determines the quantity of that element that enters into its compounds. This number, the combining-weight, or more exactly, the combining-mass, can only be determined relatively, *i.e.* that of one element must be arbitrarily fixed, those of the other elements being referred to this value.

Considered from the point of view of the atomic hypothesis, these numbers are the relative masses or weights of the atoms, and are therefore usually called atomic weights. The designation atomic mass would be more appropriate, for it is really with the mass of these material particles and not with their weight, which varies from place to place, that we are concerned. We will, however, use in the following pages the incorrect name "atomic weight," as it is now employed in all branches of chemical literature, and as no grave error is likely to arise from its use.

The determination of the relative combining or atomic weights was the most important task experimental chemistry had to undertake after the discovery of the fundamental laws of mass. For if these constants were once correctly determined, it became possible to calculate the relations of mass in all chemical compounds with this same degree of accuracy after the relative numbers of the different atoms had been ascertained by an analysis of only approximate correctness.

At first it was practically Berzelius alone who devoted himself to this task, and executed it in a comprehensive way with a degree of certainty and accuracy quite extraordinary for his time. His numbers therefore enjoyed the greatest confidence; especially on the Continent. In England somewhat different numbers were in use, in consequence of a hypothesis which will be discussed later. When these numbers, however, were subjected to a revision by Turner, the values of Berzelius were found to be confirmed in the most

striking manner, so that the confidence in the accuracy of the latter reached at this time its highest point.

Meanwhile the most careful experimenters, in the course of the analysis of organic compounds containing only carbon and hydrogen, found numbers which made the sum of the components appear greater than the quantity of substance taken. As, in the analysis, carbon is weighed as carbonic acid, and hydrogen as water, there remained nothing but to conclude that the quantity of the element in question that the one or the other contained had had a wrong value assigned to it in the calculation. Researches of Liebig and Redtenbacher, Dumas and Stas, Erdmann and Marchand, which were made to test this, all went to prove that Berzelius in his determination of the atomic weight of carbon had made a considerable error, one of about two per cent.

This wholly unexpected discovery (1840) created a perfect panic amongst chemists. The height of confidence formerly felt in the numbers of Berzelius was now equalled by the depth of distrust conceived for them, and this distrust was considerably enhanced by the position assumed by Dumas with regard to the question. An active revision of Berzelius's numbers at once commenced, the result of which was to show that this error was by far the largest, in fact almost the only one he had committed; the numerous redeterminations all confirmed the correctness of the other values found by this conscientious experimenter. Nemesis, too, soon overtook Dumas, for an extremely extensive research of his own on the atomic weight of a great number of elements was proved to be almost worthless on account of a source of error in the chief method he employed.

Since then revisions and redeterminations of the atomic weights have been steadily in progress. Twice, however, they have received a special impulse. First, a hypothesis advanced by Prout and Meinecke stating that all atomic weights were multiples of that of hydrogen incited to a great number of extremely accurate researches, in particular to those of Stas, which in this respect are unsurpassed. Again, the relation discovered by Mendelejeff and Lothar Meyer between the masses and the other properties of the atoms occasioned many investigations, for in particular cases the general relation seemed not to hold, and as a probable cause of this was the inexact determination of the atomic weights, a revision of these became necessary.

As we can at present determine the values of the atomic weights only relatively, we have in the first place to fix the unit to which they may all be referred, *i.e.* the atomic weight of one of the elements must be arbitrarily fixed equal to a certain number. Dalton adopted hydrogen as his standard, as its atomic mass was the smallest of all. Berzelius subsequently abandoned this unit from the following practical considerations. There are very few hydrogen compounds that are capable of being analysed with exactness, so that the ratio between the atomic weight of hydrogen and that of other elements can only be determined for the most part indirectly. Oxygen, on the other hand, forms very suitable compounds with nearly all the elements, and so Berzelius chose it as his standard substance, setting its atomic weight not equal to unity, but to 100, so that the other atomic weights might be of convenient magnitude. Later on, chemists returned to



Dalton's unit, because hydrogen had become in other respects a standard substance in the science. A practical difficulty has, however, arisen from this, viz. that all the values of atomic weights which have been determined with respect to oxygen—and that is the great majority—must be calculated by the aid of the ratio Hydrogen : Oxygen. This ratio is unfortunately by no means well known; the possible error in it amounts to much more than the error in a large number of atomic weights of elements compared to that of oxygen, so that by this method of calculation the results are affected with unnecessary inexactness.

It is therefore most practical to formally retain Dalton's unit, but really to return to that of Berzelius by arbitrarily setting the atomic weight of oxygen, which is very approximately sixteen times that of hydrogen, equal to 16.

This is the same mode of procedure that recommended itself as the only practical one in fixing the metric unit of length. The metre was originally intended to be a ten-millionth part of the earth's quadrant. The determination of this value, however, by geodetic measurement is susceptible of much less accuracy than the process of making copies of this length once it is determined, so that we run the danger of getting a sensibly different metre at every new measurement of arc. It was therefore agreed to accept the original measure of length kept in Paris and constructed in the above way as the real metre, and to give up its relation to the earth's quadrant altogether.

The unit of electrical resistance has been lately fixed in the same way; a value was arbitrarily chosen which differed but little from the theoretical value. This ought to be the case in chemistry likewise; all calculations in this book will therefore be made on this basis.

Of the numerous researches that have been undertaken with a view to fixing the atomic weights of the various elements only a few can be mentioned here. But at least the most important of the methods employed will be illustrated by examples.

The atomic weight of hydrogen when that of oxygen is fixed at 16 is approximately 1. The first of the more exact determinations was carried out in 1819 by Berzelius and Dulong according to a method which has since been retained by almost all other investigators. The hydrogen takes up oxygen from copper oxide to form water, which is then collected in suitable vessels, the last particles of water vapour being held back by dehydrating agents such as sulphuric acid or phosphorus pentoxide.

In these experiments 30.519 g. of water were obtained. The copper oxide, which was weighed before and after the experiment, lost 27.129 g. This represents the oxygen contained in the water; the quantity of hydrogen therefore is  $30.519 - 27.129 = 3.390$  g. In water we assume that there are two atoms of hydrogen to one of

oxygen; if the mass of the latter is 16, the following proportion will hold,  $x$  being the atomic weight of hydrogen,

$$16 : 2x = 27.129 : 3.390,$$

or

$$x = \frac{16 \times 3.390}{2 \times 27.129} = .9997.$$

Similar experiments with similar results were later performed by Dumas and by Erdmann and Marchand.

Proceeding in the reverse way, Cooke and Richards (1887) compressed hydrogen gas into a previously exhausted glass globe and burned it by means of heated copper oxide. Here the hydrogen and the water formed were weighed, the oxygen being determined by difference. This method avoids the drawback of determining the weight of the hydrogen as the difference of two much larger numbers, but it contains one source of error, viz. that pure hydrogen gas is extremely difficult to prepare, and any little impurity causes a relatively great error, as all other gases are so much heavier than hydrogen.

E. H. Keiser (1888) has, however, succeeded in avoiding this error. Metallic palladium absorbs hydrogen (but no other gas) in considerable quantity and gives it up again when gently heated. Palladium was consequently saturated in a suitable vessel with hydrogen, which was expelled by heating and then burned by means of copper oxide. Here again the hydrogen and water were weighed and the oxygen found by difference. In ten experiments 6.55880 g. hydrogen gave 58.86263 g. water, whence  $H = 1.0032$ . This number is the most probable of all those hitherto found.

Values lying near this have been obtained from the determination of the specific weights of oxygen and hydrogen, it being known that these two gases unite in the proportion of 1 : 2 by volume. The specific gravities have been ascertained at different times by different experimenters. Regnault's numbers give  $H = 1.0025$ ; new values obtained with the greatest care by Lord Rayleigh lead to  $H = 1.0055$  if we take account of the work of Scott (1887), according to which the gases do not unite in the proportion 1 : 2, but 1 : 1.9965 by volume. These values, however, are less trustworthy because the preparation of perfectly pure hydrogen is at present still an unsolved problem.

A good example of a somewhat more complicated mode of procedure for the determination of atomic weights is to be found in the method, again given by Berzelius, for chlorine, potassium, and silver, as it was afterwards employed by several chemists, in particular by Marignac and Stas.

Potassium chlorate,  $KClO_3$ , is decomposed by heat into  $KCl + 3O$ . Stas, taking in such an experiment 127.2125 g. chlorate, found 77.4023 g. potassium chloride in the residue, consequently 49.8102 g. oxygen had been driven off. Now as three atoms of oxygen are con-

tained in the potassium chlorate, we can set the following proportion, where  $x$  is the formula-weight of potassium chloride,  $\text{KCl}$ :

$$3 \times 16 : x = 49.8102 : 77.4023,$$

$$x = 74.590.$$

The formula-weight of potassium chloride is therefore 74.590, *i.e.* the sum of the atomic weights of potassium and chlorine is equal to this number.

To get the separate values from this the formula-weight of silver chloride was obtained by its aid. For this purpose a known quantity of potassium chloride was precipitated by excess of silver solution and the silver chloride washed and weighed. In this way Marignac (1846) obtained from 14.427 g. potassium chloride 27.732 g. silver chloride, so that the formula-weight of the latter may be found from the proportion

$$74.590 : x = 14.427 : 27.732$$

to be

$$x = 143.39.$$

Lastly, the ratio of chlorine to silver in silver chloride was determined by the transformation of a known weight of silver into silver chloride, the weight of which was also observed. This transformation can be brought about in various ways; we can heat the silver in a stream of chlorine, when it goes directly into silver chloride, or we may first dissolve it in nitric acid so that it becomes silver nitrate, which is then converted into silver chloride by precipitation with hydrochloric acid, ammonium chloride, or any other suitable compound of chlorine. The same ratio between silver and silver chloride is always obtained, no matter which process we adopt. From such experiments I select one by Stas, who found that 101.519 g. silver gave after heating in a stream of chlorine 134.861 g. silver chloride. As the formula-weight of the latter was found above equal to 143.39, we get the atomic weight of silver from the proportion

$$143.39 : x = 134.861 : 101.519,$$

$$x = 107.94.$$

The atomic weight of silver is consequently  $\text{Ag} = 107.94$ . From this follows further, since  $\text{AgCl} = 143.39$ , that the atomic weight of chlorine is  $143.39 - 107.94 = 35.45$ . Lastly, if we subtract this value  $\text{Cl} = 35.45$  from the number obtained in the first series,  $\text{KCl} = 74.59$ , the atomic weight of potassium follows as  $\text{K} = 39.14$ .

The most exact and trustworthy of such researches are those of J. S. Stas (1860-65), which comprehend the elements silver, chlorine, bromine, iodine, potassium, sodium, lithium, sulphur, nitrogen, and lead. With the first four elements he altered the method of Berzelius in so far as he decomposed, for example, silver chlorate,  $\text{AgClO}_3$ , instead of potassium chlorate. In this way he arrived directly at the formula-weight of silver chloride, and, by determination of the ratio between chlorine and silver, at the atomic weights of these two elements.

Similar operations with silver bromate and iodate, combined with the determination of the ratios of the elements in silver bromide and iodide, gave the values for bromine and iodine as well as two new and completely independent values for silver. It is in the highest degree noteworthy that these values for the atomic weight of silver, though totally independent of each other and obtained from different substances, agree in the most perfect manner. This forms, indeed, one of the best evidences of the excellence of the atomic hypothesis.

For sulphur Stas adopted the following method. On the one hand he reduced silver sulphate,  $\text{Ag}_2\text{SO}_4$ , by means of hydrogen to silver; on the other he transformed silver by means of sulphur into silver sulphide,  $\text{Ag}_2\text{S}$ . The calculation of the results is as follows:—150·000 g. silver heated in sulphur vapour gave 172·2765 g. silver sulphide; consequently 100 parts of silver combine with 14·851 of sulphur. On the other hand 56·071 g. silver were obtained from 81·023 g. silver sulphate. Now, as the ratio of silver to sulphur in silver sulphate and in silver sulphide is the same, it follows that along with the 56·071 g. silver in the 81·023 g. sulphate there must be 8·3275 g. sulphur. The remainder, 16·6247 g., is oxygen. The mass of the four atoms of oxygen contained in the sulphate must therefore be to that of the one atom of sulphur as 16·6247 : 8·3275, and so we have

$$\begin{aligned} 4 \times 16 : x &= 16\cdot6247 : 8\cdot3275, \\ x &= 32\cdot06, \end{aligned}$$

*i.e.* the atomic weight of sulphur is  $S = 32\cdot06$ .

For the three alkali metals Stas employed the method of silver titration, originally worked out for quite another purpose by Gay-Lussac, and used for the first time by Pelouze (1845) in atomic-weight determinations.

If a silver solution be added in small quantities at a time to the solution of a chloride, we can easily tell the moment when all the chlorine has gone into silver chloride by a further drop of silver solution producing no cloudiness in the liquid which has been made clear by shaking and allowing to stand.

For example, 10·5249 g. sodium chloride were weighed out; this required a quantity of silver solution which contained 19·4160 g. silver dissolved in nitric acid. If  $x$  be the formula-weight of sodium chloride, it follows, as 107·94 is that of silver, that

$$\begin{aligned} x : 107\cdot94 &= 10\cdot5249 : 19\cdot4160, \\ x &= 58\cdot510. \end{aligned}$$

In this way then the value for the chloride is obtained; if the atomic weight of chlorine, 35·45, be subtracted from this, then we have that of sodium,  $\text{Na} = 23\cdot06$ . In a similar way that of lithium was found to be  $\text{Li} = 7\cdot030$ .

For nitrogen Stas used a method first given by Penny (1839). A

weighed quantity of potassium chloride was by repeated evaporation with nitric acid changed into potassium nitrate. In one experiment 48·9274 g. potassium chloride gave 66·3675 g. potassium nitrate. If  $x$  be the formula-weight of the latter, and if that of potassium chloride is 74·59 (p. 16), we get

$$\begin{aligned}x : 74\cdot59 &= 66\cdot3675 : 48\cdot9274, \\x &= 101\cdot175.\end{aligned}$$

Since potassium nitrate has the formula  $\text{KNO}_3$ , we must subtract from this number  $\text{K} = 39\cdot14$  and  $3\text{O} = 48\cdot00$ , whence follows  $\text{N} = 14\cdot04$ . Similar researches with the same result were made by Stas with sodium and lithium chlorides.

Another and more simple process consisted in transforming silver into silver nitrate. In one such experiment 77·2684 g. silver gave 121·6749 g. nitrate, whence, according to the proportion

$$\begin{aligned}x : 107\cdot94 &= 121\cdot6749 : 77\cdot2684, \\x &= 169\cdot97,\end{aligned}$$

the formula-weight of silver nitrate,  $\text{AgNO}_3$ , is 169·97, and from this, by subtracting  $\text{Ag} = 107\cdot94$  and  $3\text{O} = 48\cdot00$ , we get the atomic weight of nitrogen  $\text{N} = 14\cdot03$ .

The experiments described above give examples of the different general methods adopted for the determination of atomic weights. In the following pages short notices of the methods employed in each case and the most accurate of the numbers obtained are given for all the elements:—

1. *Aluminium*.—Berzelius in 1812 obtained the number  $\text{Al} = 27\cdot32$  by igniting aluminium sulphate. With this result derived from a single experiment at the very beginning of such researches the chemical world was content for over thirty years, till Tissier (1858), and after him many others, determined the constant anew. The number at present recognised as correct was obtained by Mallet (1880), who from the ignition of crystallised ammonium alum ( $2\text{NH}_4\text{AlS}_2\text{O}_8 \cdot 12\text{H}_2\text{O} : \text{Al}_2\text{O}_3$ ) found  $\text{Al} = 27\cdot12$ , by titration of aluminium bromide with silver solution  $\text{Al} = 27\cdot11$ , by combustion of the hydrogen evolved by weighed quantities of aluminium from potash ( $2\text{Al} : 3\text{H}_2\text{O}$ )  $\text{Al} = 27\cdot05$ , and by measurement of the hydrogen got in the same reaction  $\text{Al} = 27\cdot04$ .  $\text{Al} = 27\cdot08$  may be accepted as the most probable value of the atomic weight.

2. *Antimony*.—The atomic weight of this element was till 1856 only roughly known. By reduction of natural antimony glance from Arnsberg by means of hydrogen ( $\text{Sb}_2\text{S}_3 : 2\text{Sb}$ ) Schneider (1856) obtained  $\text{Sb} = 120\cdot6$ . It is true that Dexter at the same time got higher numbers by oxidation of antimony to tetroxide by means of nitric acid ( $2\text{Sb} : \text{Sb}_2\text{O}_4$ ), these being apparently confirmed by Dumas's titration experiments with antimony chloride and silver solution; but a thorough investigation by Cooke (1880) proved that Schneider's number was correct. The error in the determinations of Dumas lies in the fact that such easily decomposable chlorides as antimony chloride are scarcely ever to be obtained in a state of purity. The least trace of aqueous vapour forms oxychloride, while hydrochloric acid escapes, and

the oxychloride cannot be completely separated from the chloride by distillation. Consequently the preparation contains too little chlorine and the atomic weight comes out too high.

The experiments of Cooke consisted of syntheses of antimony sulphide ( $2\text{Sb}:\text{Sb}_2\text{S}_3$ ), determinations of the bromine in antimony bromide ( $\text{SbBr}_3:3\text{AgBr}$ ), titrations of antimony bromide with silver solution ( $\text{SbBr}_3:3\text{Ag}$ ), and determinations of the iodine in antimony iodide ( $\text{SbI}_3:3\text{AgI}$ ). The mean is  $\text{Sb} = 120.2$ .

This number has been since repeatedly confirmed. Experiments on a new principle were performed by Pfeifer (1881) and Popper (1887). According to Faraday's law of electrolysis (see below), the same current separates from different electrolytes equivalent quantities of their components. If a current, therefore, be passed through a silver and an antimony solution successively, the deposited quantities of the metals must be in the proportion of their "equivalents," *i.e.* in the proportion  $\text{Sb}:3\text{Ag}$ . In this way  $\text{Sb} = 120.7$  was found. A series of experiments by Bongartz (1883), in which the sulphur in antimony sulphide was transformed into barium sulphate, yielded the value  $\text{Sb} = 120.1$ . We may look upon  $\text{Sb} = 120.3$  as the most probable mean.

3. *Arsenic*.—This element has been the subject of but few researches. An interesting method was employed by Berzelius (1818), who heated arsenic trioxide with excess of sulphur. The loss of weight from the escaping sulphur dioxide ( $2\text{As}_2\text{O}_3 + 9\text{S} = 2\text{As}_2\text{S}_3 + 3\text{SO}_2$ ) yields the needful relations. The number at present accepted was obtained by Pelouze (1845) and Dumas (1859) by titration of arsenic trichloride with silver solution, and is  $\text{As} = 75.0$ .

4. *Barium*.—The atomic weight of barium was determined first by Berzelius (1811) from the transformation of the carbonate into the sulphate ( $\text{BaSO}_4:\text{CO}_2$ ), later by him and many others (Turner 1829, Pelouze 1845, Marignac 1848 and 1858, Dumas 1859) by means of the precipitation of the chloride by silver solution. Besides these processes there are a few other less exact methods which need no mention here. The mean of the best determinations gives  $\text{Ba} = 137.0$ .

5. *Beryllium*.—The analysis of beryllium sulphate is almost the only method. Along with the older and not so exact experiments of Berzelius (1815 and 1826), Awdejef (1842), Weeren (1854), Debray (1855), Klatzo (1869), we possess very good determinations by Nilson and Pettersson (1880), who performed the analysis of the sulphate in the simplest possible way, namely by strong ignition, when  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  became  $\text{BeO}$ . The result was  $\text{Be} = 9.10$ .

6. *Bismuth*.—For the atomic weight of this metal an incorrect value has almost always been in use. The experiments of Lagerhjelm (1816) had given too high results, and though Schneider (1851) by oxidation of the metal had fixed the value rightly at 208, yet on the authority of Dumas, who obtained (1859) too high results by the method of silver titration, the wrong figures were used almost exclusively. Only recently have they been given up, as both Löwe (1883) by oxidation of the metal and Marignac (1883) by transformation of the oxide into the sulphate and by reduction of the oxide to metal in a current of hydrogen, found a smaller number, in agreement with Schneider's determination. The mean of these numbers is  $\text{Bi} = 208.0$ .

7. *Boron*.—To determine this atomic weight Berzelius (1824) established the percentage of water in crystallised borax, whence follows  $B = 11.01$ . With this number we must still be content, as some analyses of the chloride and bromide by Deville (1859) gave numbers which did not sufficiently agree among themselves.

8. *Bromine*.—The older determinations of the atomic weight of bromine by Balard (1826) and Liebig (1826) give too low results, as the material was not free from chlorine. Berzelius obtained a better value by heating silver bromide in a stream of chlorine, when it was converted into silver chloride. Marignac executed a series of experiments  $KBrO_3 : KBr$ ,  $KBr : AgBr$ ,  $Ag : Br = AgBr$ —exactly similar to that described on p. 15, only bromine occupied the place of chlorine. The result was  $Br = 79.96$ .

Stas, finally, reduced silver bromate to bromide, and determined the ratio  $Ag : Br$  in the latter. His experiments were executed on a much larger scale and with much more extensive resources than Marignac's; yet both series gave quite the same result, Stas's number being 79.963.

9. *Cadmium*.—Up to the year 1857 a number was used for the atomic weight of cadmium which rested on a single datum given by the discoverer Stromeyer (1818), but which was afterwards shown to be tolerably accurate. Of the later investigators, von Hauer (1857) converted cadmium sulphate into sulphide by ignition in a current of hydrogen sulphide; Dumas (1859) titrated the chloride with silver; Leussen (1860) analysed cadmium oxalate; and lastly Huntington (1881) analysed the bromide both gravimetrically and volumetrically by converting it into silver bromide. The mean of his determinations, which may be looked upon as the most exact, gives  $Cd = 112.1$ .

10. *Cesium*.—The number for this element has been determined exclusively by weighing the silver chloride obtained from a given quantity of cesium chloride. The most exact experiments are by Godeffroy (1876), and give  $Cs = 132.9$ .

11. *Calcium*.—Although calcium occurs in the earth's crust in greater quantity than any other metallic element, its atomic weight is nevertheless not known with a certainty corresponding to its importance. Berzelius at the very beginning of his researches (1811) performed one single analysis of calcium chloride, and with the number calculated from this, chemists were satisfied for the next thirty years, when Dumas (1842) made some determinations by igniting Iceland spar ( $CaCO_3 : CaO$ ). Thereupon Erdmann and Marchand undertook a long investigation (1842-50), employing various methods, the final result of which was a single faultless experiment on the loss of calcium carbonate when ignited. This gave  $Ca = 40.0$ . The uncertainty which exists as to this value is not diminished by a series of experiments made by Dumas, who titrated calcium chloride with silver, as the preparation of the chloride quite free from oxide presents great difficulties, which Dumas does not prove himself to have overcome. Meanwhile we must retain the value  $Ca = 40.0$ .

12. *Carbon*.—The determination of the atomic weight of this element was at first founded by Berzelius on the observation that oxygen does not increase in volume when it changes into carbon dioxide; therefore the atomic weight of oxygen is to that of carbon dioxide as the specific gravities of the two gases. This is not, however, strictly correct; the volume of the

carbon dioxide is somewhat smaller than that of the oxygen, and a false value thus arose which was only corrected in 1841 by the researches of Liebig and Redtenbacher, of Dumas and Stas, and of Erdmann and Marchand (p. 13). The value  $C = 12.00$  found by these chemists has been confirmed several times by later investigators, *e.g.* by Stas (1849) from the combustion of carbon monoxide, by Roscoe (1882) from the combustion of Cape diamonds, and lastly by van der Plaats (1885), who burned sugar charcoal, graphite, and paper charcoal. Therefore we may put with great certainty  $C = 12.00$ .

13. *Cerium*.—The determination of the atomic weight of this element has been one of uncommon difficulty. The difficulty lay, not so much in the analytical methods, but rather in the separation of the cerium compounds from those of the other earths which accompany them. It is on account of this circumstance that different chemists, working with equal care, have arrived at very different results.

The oldest determinations by Hisinger (1816) were made at a time when lanthanum and didymium, which always accompany cerium, were not yet discovered. Beringer (1842) was the first to work with anything like pure preparations. He analysed the chloride and sulphate. Later researches by Hermann, Rammelsberg, Marignac, Jegel, Wolf, and Bührig showed that according to the origin and method of purification of the cerium preparations employed, very different atomic weights (between 130 and 140) are obtained. Only recently have Robinson (1884) and Brauner (1885) obtained concordant results with carefully purified material in quite independent researches. The method was that of converting the sulphate into the oxide by ignition, and the result obtained was  $Ce = 140.2$ .

14. *Chlorine*.—The method first employed by Berzelius has already been given on p. 15, and by its means the atomic weight of this element has finally been fixed. The number of investigators, from Berzelius to Stas, who have proved their strength on this task has been very large, the most exact results besides those already mentioned being obtained by Penny (1839) and Marignac (1842-46). Other methods were, it is true, attempted, but they met with no success. Marignac, for instance, obtained very inaccurate results by heating copper oxide in a stream of hydrochloric acid gas ( $CuO + 2HCl = CuCl_2 + H_2O$ ); and the results of the analysis of a complicated organic compound, by which method Laurent (1842) sought to solve the problem, are just as little worthy of confidence. The number at present considered correct is that found by Stas, from which the older determinations of Marignac, Penny, and Berzelius differ but slightly. It is  $Cl = 35.453$ .

15. *Chromium*.—The atomic weight of this element must be classed with those which have not been quite firmly established by a thorough investigation. Berzelius in 1818 made some analyses of lead chromate and barium chromate, the results of which were much further removed from the truth than was usual with this exact worker. Berlin (1846), who transformed silver chromate into silver chloride and chromic oxide, found the wished-for number with sufficient approximation. Later researches by Moberg (1848), Lefort (1850), Wildenstein (1853), and Kessler (1861), in which different and mostly unsuitable methods were employed, are inferior to the work of Berlin. Siewert (1861) drew attention to a source of error in Berlin's determination, supposed to be caused by the slight solubility of silver chloride



in the acid chromic solution from which it was precipitated; by avoiding this he obtained 52.1 instead of Berlin's 52.5. Baubigny (1884) found a value between these two from the transformation of chromic sulphate into chromic oxide by strong ignition. This value,  $\text{Cr} = 52.2$ , must be taken as the most probable.

16. *Cobalt*.—A great number of researches have been undertaken with this element, especially for the purpose of deciding whether cobalt and nickel have the same or different atomic weights, and for no element have different but equally trustworthy investigators obtained such widely divergent results. The chief names are Rothoff (1818), Schneider (1857), Marignac (1857), Gibbs (1858), Dumas (1859), Russell (1863 and 1869), Sommaruga (1866), Winkler (1867), Weselski (1868), Lee (1871), Zimmermann (1886). The methods applied were very different, and the results vary between  $\text{Co} = 58.8$  and 60.6. Just lately (1889) Krüss seems to have found the cause of this unusual disparity, in that cobalt and nickel in their ores are always accompanied by a metal hitherto unknown, the presence of which in varying proportions has rendered the preparations of these metals impure. Under such circumstances none of the older determinations may be used, and the further results of the discoverer must be awaited.

17. *Copper*.—Most experiments towards the determination of the atomic weight of this metal have been executed by the reduction of a weighed quantity of cupric oxide heated in hydrogen. Simple as the method appears, yet it is affected with an error having its source in the fact that the spongy reduced copper condenses sensible quantities of hydrogen on its surface, thus increasing its weight. According to this method we have researches by Berzelius (1820), Erdmann and Marchand (1844), Millon and Commaille (1864), and Hampe (1874). The last mentioned further determined the copper in anhydrous copper sulphate by electrolytic deposition. Baubigny (1883) transformed copper sulphate into oxide by ignition.

By quite another method, similar to that adopted for antimony (p. 19), W. N. Shaw (1887) has determined the value in question. He passed an electric current through two solutions, one of which deposited copper and the other silver, and by Faraday's Law determined the equivalent and the atomic weights of copper from his results. The number he obtained agrees very closely with that got by the purely chemical methods, the most probable value being  $\text{Cu} = 63.3$ .

18. *Didymium*.—The same observations as were made on cerium (p. 21) apply also to this element. The old data of Marignac (1849 and 1853), Hermann (1861), Zschiesche (1869), and Erck (1870) all vary greatly. They were mostly obtained from the precipitation of didymium sulphate by barium chloride, and are affected with an error caused by the barium sulphate under these conditions taking down with it considerable quantities of didymia by surface attraction. However, experiments of Cleve, Nilson and Pettersson, and Brauner, who all converted the sulphate into the oxide by ignition, yielded discordant numbers in spite of the identical methods. In 1885 Auer von Welsbach reported that he had split the "element" hitherto known as didymium into two others, which he called praseodymium and neodymium. The atomic weights are, according to the preliminary experiments, which have not yet been confirmed,  $\text{Pr} = 143.6$  and  $\text{Nd} = 140.8$ .

19. *Erbium*.—For this rare element also the difficulty of purification is very great. As the substance has become investigated more thoroughly, more and more elements with different properties have been separated from it, so that we have at present no guarantee that what we call erbium is really a single uniform substance. The last determinations by Cleve (1880) gave  $\text{Er} = 166$ .

20. *Fluorine*.—The atomic weight of fluorine had been fixed for a long time before the element itself was known in the free state, a discovery of only recent date. It was only known as a constituent of various compounds, and its existence was inferred from the fact that these compounds are different from all compounds of known elements. For the determination of the atomic weight one method has been used almost exclusively, viz. the conversion of calcium fluoride into calcium sulphate by evaporation with sulphuric acid— $\text{CaF}_2 + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + 2\text{HF}$ . Such experiments were executed by Berzelius (1818 and 1824), Louyet (1849), Dumas (1859), de Luca (1862) with somewhat varying results, as calcium fluoride is decomposed completely by sulphuric acid only with extreme difficulty. Consequently other compounds, such as sodium and lead fluoride, were used by some investigators. The mean of the good experiments is  $\text{F} = 19.00$ . This number has been lately confirmed in another way. Christensen (1886) decomposed the compound  $(\text{NH}_4)_2\text{MnF}_5$ , which crystallises well, with hydriodic acid  $((\text{NH}_4)_2\text{MnF}_5 + \text{HI} = 2\text{NH}_4\text{F} + \text{MnF}_2 + \text{HF} + \text{I})$  and determined the liberated iodine volumetrically by means of sodium thiosulphate. The result was the same,  $\text{F} = 19.00$ .

21. *Gallium*.—Lecoq de Boisbaudran, the discoverer of gallium, determined its atomic weight by igniting ammonium gallium alum,  $\text{NH}_4\text{GaS}_2\text{O}_8 + 12\text{H}_2\text{O}$ , when gallium oxide,  $\text{Ga}_2\text{O}_3$ , remained behind. He also converted the metal into oxide. The result is  $\text{Ga} = 69.9$ .

22. *Germanium*.—The discoverer of germanium, Cl. Winkler, analysed germanium chloride,  $\text{GeCl}_4$ , by decomposition with sodium carbonate, and volumetric estimation of the chlorine by means of silver solution. From his data we get  $\text{Ge} = 72.3$ .

23. *Gold*.—A great many methods have been applied to this element. First of all Berzelius (1813) precipitated a solution of gold with mercury and thus determined the ratio of the atomic weights of the two metals. Javal (1821) obtained quite other numbers by analysis of auric oxide, whereupon Berzelius (1845) determined the ratio between chlorine and gold in a neutral solution of auric chloride, as well as that between gold and potassium chloride, by igniting potassium auric chloride,  $\text{KAuCl}_4$ , in a current of hydrogen. Levol (1850) worked according to a completely different method; he reduced a solution of auric chloride with sulphur dioxide ( $2\text{AuCl}_3 + 3\text{SO}_2 + 6\text{H}_2\text{O} = 2\text{Au} + 3\text{H}_2\text{SO}_4 + 6\text{HCl}$ ) and determined the ratio between the gold and the barium sulphate precipitated from the solution by barium chloride. G. Krüss, and Thorpe and Laurie have lately (1887) undertaken new determinations by the last method of Berzelius, *i.e.* by the decomposition of double salts of gold, and find in the mean  $\text{Au} = 197.2$ .

24. *Indium*.—This element has been investigated as to its atomic weight by its discoverers, Reich and Richter (1864), by Winkler (1867), and by Bunsen (1870). The method principally employed consisted in the oxidation of the metal to oxide. The value obtained was  $\text{In} = 113.7$ .

25. *Iodine*.—Gay-Lussac (1814), to whom we owe our exact knowledge of this element, determined the ratio in which iodine and zinc combine. Berzelius (1828) decomposed weighed quantities of silver iodide by heating them in a current of chlorine, when they are completely converted into silver chloride, and these experiments were repeated later by Dumas (1859) with exactly the same results. A method similar to that introduced by Berzelius for chlorine (p. 15) was employed by Millon (1843), who transformed potassium iodate into potassium iodide by heating. Marignac (1843) established the ratio between potassium iodide and silver, as well as that between silver and silver iodide.

Stas, finally, analysed silver iodate by decomposition by heat and absorption of the liberated oxygen by means of red-hot copper. He also determined the ratio between iodine plus silver, and silver iodide. From his experiments, with which those of Marignac are in complete concordance, it results that  $I = 126.86$ .

26. *Iridium*.—From the year 1828 until 1878—for fully fifty years—the scientific world contented itself with a single analysis by Berzelius of potassium iridium chloride. In the last-mentioned year Seubert made a most careful investigation by the same method, the result being  $Ir = 193.2$ .

27. *Iron*.—Berzelius at first (1811) gave a value for the atomic weight of iron which was considerably too low. Stromeyer (1826) and Wackenroder (1844) drew attention to the error, whereupon Berzelius caused a new investigation to be undertaken by Svanberg and Norlin (1846), to which he added some determinations of his own. These, as well as the experiments of Erdmann and Marchand (1844), Maumené (1850), and Rivot (1850), were so arranged that on the one hand pure iron was converted into oxide by treatment with nitric acid, evaporation, and ignition, and on the other hand pure oxide was converted into the metal by heating in a current of hydrogen. The results, which agree very closely, give  $Fe = 56.00$ .

28. *Lanthanum*.—The atomic weight of this element suffers from the same uncertainty as that of the other rare earths. The numerous investigators who have occupied themselves with its determination will therefore not be named, especially as the methods used were always the same. As the most probable value we may take that given by Cleve (1883), viz.  $La = 138.5$ .

29. *Lead*.—Lead takes a prominent place in the history of atomic weights, as being the first element on which Berzelius (1811) exercised his skill. His method consisted in the treatment of metallic lead with nitric acid and subsequent ignition of the nitrate, lead monoxide remaining. He afterwards analysed lead chloride (1818), and reduced lead oxide by means of hydrogen (1830). Turner (1833) converted lead and lead oxide into sulphate, Marignac (1858) and Dumas (1859) titrated lead chloride with silver solution. The value at present in use we owe to Stas, who in two series of experiments converted lead into lead nitrate and into lead sulphate. The mean of his experiments gives  $Pb = 206.91$ .

30. *Lithium*.—Very divergent results have been obtained by different chemists in the determination of the atomic weight of this metal. The discoverer Arfvedson (1818) gave  $Li = 10.3$ . Vauquelin (1818) then found  $Li = 9.2$ , Gmelin (1818) 10.8, Kralovanszky (1827) 10.6; on the other hand Hermann (1829) 6.1, Berzelius (1830) 6.6, Hagen (1839) 6.5, Mallet

(1857) 6.95. Troost, who had before given wrong figures, was the first (1862) to determine the value with approximate correctness. The exact number was then found by Diehl (1862), who decomposed a weighed quantity of lithium carbonate with sulphuric acid and determined the carbon dioxide from the loss of weight of the whole apparatus. Stas, in conclusion, determined by titration the ratio between lithium chloride and silver, and obtained the present number,  $\text{Li} = 7.03$ .

31. *Magnesium*.—Most of the old determinations were made from the analysis or synthesis of the sulphate, *e.g.* by Berzelius (1812), Gay-Lussac (1819), Scheerer (1846), Svanberg and Nordenfeldt (1848), Jacquelin (1850), Bahr (1852). The determination by Bahr is particularly interesting, as being made with a specimen of magnesia obtained from the olivine of a Siberian meteorite. This celestial magnesia proved to be identical with the ordinary terrestrial substance in respect of the atomic weight, as it was in all other properties.

An extensive investigation by Marchand and Scheerer (1850) into the quantity of carbon dioxide contained in natural magnesium carbonate (magnesite from Frankenstein) is unfortunately valueless, as Scheerer nine years later discovered that the material employed contained calcium. The experiments of Dumas (1859) on the ratio between magnesium chloride and silver only showed the inapplicability of the method, for in spite of heating in a current of hydrochloric acid, it was found impossible to prepare magnesium chloride perfectly free from oxygen. Marignac has lately (1883) obtained results by means of the old method of analysis and synthesis of the sulphate which satisfy the requirements justly expected of a constant so frequently in use. He found  $\text{Mg} = 24.38$ . The number even yet almost always employed,  $\text{Mg} = 24.00$ , is thus over 1.5 per cent wrong.

32. *Manganese*.—The older values for the atomic weight of manganese were somewhat uncertain; Hauer (1857) was the first to give accurate numbers, which he obtained by converting manganese sulphate into sulphide by ignition in a current of sulphuretted hydrogen. This method is much better than that again used by Dumas, *viz.* the titration with silver, as the impossibility of obtaining pure chloride became once more apparent. A series of experiments by Schneider (1859), who subjected the oxalate to combustion, is also not quite faultless. Dewar and Scott (1883) analysed silver permanganate,  $\text{AgMnO}_4$ , and Marignac (1883) converted manganous oxide into the corresponding sulphate. Both methods gave results agreeing with each other and with those of Hauer, so that we may put  $\text{Mn} = 55.0$ .

33. *Mercury*.—There has never been much doubt as to the atomic weight of this metal, as even the oldest analyses of mercuric oxide by Sefström give a number very near the right one. Later determinations have been made by different methods. Turner (1833) analysed, besides mercuric oxide, mercuric and mercurous chlorides by ignition with lime, Erdmann and Marchand (1844) reduced mercuric oxide with charcoal and mercuric sulphide with metallic copper, Millon (1846) and Svanberg (1848) repeated the decomposition of mercuric chloride by heating with lime. As mean of all the more trustworthy determinations we may take  $\text{Hg} = 200.4$ .

34. *Molybdenum*.—The oldest experiments of Berzelius (1818) were on

the conversion of lead nitrate into lead molybdate, and gave much more correct numbers than those of Svanberg and Struve (1848), who transformed the sulphide,  $\text{MoS}_2$ , into the oxide,  $\text{MoO}_3$ , by roasting. In this process there is a loss of weight of only some 10 per cent, so that the errors of experiment have a great influence on the result. Dumas (1859), on the other hand, obtained good numbers by reducing the strongly heated trioxide in a stream of hydrogen to the metallic state. The analysis of the chlorides of molybdenum by Liechti and Kämpe (1873) may also be used, and lately von der Pfordten (1884) has found the same value from the analysis of ammonium molybdate. The mean is  $\text{Mo} = 95.9$ .

35. *Nickel*.—Almost all the chemists who attempted to fix the atomic weight of cobalt have at the same time extended their investigations to nickel and found here also very varying results— from 58.0 to 59.4. The cause of this is the same as that given in the case of cobalt (p. 22), and a correct value cannot at present be stated.

36. *Niobium*.—The investigation into the nature of this element was attended with considerable difficulties, which Rose, who busied himself many years with it, did not succeed in overcoming. Blomstrand was the first to get a proper grasp of the subject, and to him we owe the determinations which may be taken as the most exact. The analysis of the pentachloride gave  $\text{Nb} = 94.2$ .

37. *Nitrogen*.—A great many different methods have been used for this element. Berzelius (1811) determined the ratio between ammonium chloride and silver chloride. He afterwards used the proposition that the specific gravities of the gaseous elements are proportional to their atomic weights (see below), and based the number considered by him as correct on weighings of oxygen and nitrogen which he executed in conjunction with Dulong (1820). Turner (1833) determined the ratio between silver nitrate and chloride, between barium nitrate and sulphate, as well as between lead nitrate and sulphate.

Penny (1839), who made his admirably exact determinations with the simplest imaginable apparatus, converted potassium chlorate into potassium nitrate by evaporation with nitric acid, and in the same way potassium chloride into nitrate, and conversely. He also deduced the atomic weight of nitrogen from the ratio between silver and its nitrate, as well as between the nitrate and chloride. His results agree almost absolutely with those of Stas, the most accurate that we have.

In spite of their excellence, Penny's results remained almost neglected, and a much less correct value given by Berzelius was used until Dumas and Boussingault showed its inaccuracy from the comparative weights of oxygen and nitrogen. Berzelius then caused a new determination to be made by Svanberg (1842), who converted lead into lead nitrate, without, however, obtaining very exact results. Good numbers were obtained by Pelouze, (1843), who titrated ammonium chloride with silver; by Marignac (1842), from the transformation of silver into silver nitrate; and by Regnault (1845), from his gas-density determinations.

Our present exact knowledge is due to the work of Stas, already referred to (p. 17). His mean value is  $\text{N} = 14.041$ .

38. *Osmium*.—For this element too a single analysis of potassium

osmium chloride by Berzelius (1828), which gave  $\text{Os} = 200$ , had to serve until quite recently. Seubert in 1888 made an exact determination by the analysis of ammonium and potassium osmium chlorides, and this led to a much smaller value, which must be considered correct, viz.  $\text{Os} = 192$ .

39. *Palladium*.—The case is at present the same for palladium as it was with osmium until a year ago; our whole knowledge of its atomic weight is confined to two experiments by Berzelius in the year 1828, who analysed potassium palladium chloride. We can, therefore, place but little reliance on his result,  $\text{Pd} = 106$ .

40. *Phosphorus*.—For the determination of the atomic weight of this element many methods were tried by Berzelius without satisfactory results. Jacquelin's methods (1852) as well as his numbers were still more diversified. Schrötter (1852) obtained trustworthy results, and these are still the best we know. He burned weighed quantities of red phosphorus (of which he was the discoverer) with oxygen to phosphorus pentoxide in a suitable apparatus. Similar experiments have been recently made by van der Plaats (1885), who obtained the same results.

Pelouze (1845) and Dumas (1859) applied the method of silver titration to the trichloride; here again the usual difficulty of obtaining pure chloride, in this case chloride free from oxychloride, was encountered. The numbers are therefore almost all too high.

Schrötter's experiments give  $\text{P} = 31.03$ .

41. *Platinum*.—The ill luck which followed Berzelius in his determination of the atomic weight of the platinum metals—a want of success in striking contrast to the great trustworthiness of his other experiments—is found here in the case of platinum itself. The older data (1813 and 1826) which he obtained from the precipitation of a platinum solution by means of mercury and from the analysis of platinous chloride were rejected by him in favour of a number,  $\text{Pt} = 197.2$ , based on the analysis of potassium platinic chloride, although they were much nearer the truth. In 1881 Seubert showed a considerable error to exist in this determination, and from the analysis of potassium and ammonium platinic chlorides obtained the number  $\text{Pt} = 194.8$ . This difference is not unimportant, for in the analysis of substances containing nitrogen this element is very often separated as ammonium platinic chloride and calculated from the residue of platinum left on heating. Up to 1881, therefore, the analyses made according to this method are affected with an error which makes the nitrogen appear less than it really is.

42. *Potassium*.—With exception of the very oldest experiments of Berzelius (1811), who converted metallic potassium (weighed as amalgam) into potassium chloride, the atomic weight of this metal has always been determined along with that of chlorine by the analysis of potassium chlorate. The different investigators who have taken part in this work are named on p. 21. The number at present in use is that of Stas,  $\text{K} = 39.14$ .

43. *Rhodium*.—The number obtained by Berzelius (1828) from the analysis of sodium rhodium chloride appears to be somewhat more correct than those of the other platinum metals, for it has only been altered a unit by the new determinations of Jörgensen (1883), whose experiments, however, have only a preliminary character—according to them  $\text{Rh} = 103$ .

44. *Rubidium*.—The new alkali metals rubidium and cesium were dis-

covered by Bunsen as the first-fruits of spectrum analysis. While the complete purification of caesium did not succeed at once, rubidium was very soon obtained free from admixed substances, and the number got from the analysis of the chloride (1861) has been confirmed by similar determinations due to Piccard (1862) and Godeffroy (1875). The mean is  $Rb = 85.1$ .

45. *Ruthenium*.—The discoverer of this metal, Claus, to whose work we owe almost our whole knowledge of the element, determined its atomic weight by the analysis of potassium ruthenium chloride,  $K_2RuCl_5$ . The result was  $Ru = 103.8$ . Joly has lately found a considerably smaller value, viz.  $Ru = 101.7$ .

46. *Samarium*.—This element is still less certainly a single pure substance than the other metals of the rare earths. Cleve (1884), who converted the oxide into sulphate, gives the value  $Sm = 150$ .

47. *Scandium*.—This element also belongs to the "rare earths," but it is far more probably a pure substance than the others, from which it differs very decidedly by its small atomic weight. Nilson (1880), who discovered it simultaneously with Cleve, gives  $Sc = 44.1$  from the conversion of the oxide into sulphate.

48. *Selenium*.—The determination of the atomic weight of selenium has been attended with considerable difficulty. Berzelius (1818) employed a quite unusual process—the conversion of weighed quantities of selenium into the tetrachloride,  $SeCl_4$ —and placed more confidence in the number got in this way than in those from the analysis of silver selenide and barium seleniate. A publication of Sacc (1847) contains merely a list of unsuccessful experiments. A short report of the analysis of mercury selenide is due to Erdmann and Marchand (1852). Dumas finally repeated (1859) the experiments of Berzelius on the formation of the tetrachloride.

The number at present in use is founded on an investigation by Ekman and Pettersson (1876) in which on the one hand selenium was converted into the dioxide, and on the other silver selenite transformed into silver chloride. The mean is  $Se = 79.1$ .

49. *Silicon*.—The atomic weight of this element was known before the element itself. Berzelius (1810) and with better success Stromeyer (1811) prepared iron rich in silicon, and oxidised weighed quantities of this. The product of oxidation was analysed, and after subtraction of the iron from the original substance and of the iron oxide from the product, the ratio of silicon to silicon dioxide was obtained. Berzelius afterwards investigated various silicates, both natural and artificial, as well as barium silicofluoride, without, however, obtaining satisfactory results.

The application of silver titration yielded accurate numbers. After the first experiments by Pelouze (1845), the process was applied by Dumas (1859) and Schiel (1861) with the same results. Thorpe and Young have lately (1887) decomposed weighed quantities of silicon tetrabromide with water and weighed the resulting silica. The result is  $Si = 28.4$ .

50. *Silver*.—The atomic weight of silver has always been determined simultaneously with those of chlorine and potassium, so that the data given on p. 15 may be referred to. The number at present accepted, and it must be considered the best known of all the atomic weights, was determined

by Stas according to five independent methods, the results of which here follow—

- a.* Analysis of potassium chlorate and determination of the  
ratio KCl : Ag . . . . . 107·940
- b.* Analysis of silver chlorate and synthesis of silver chloride . . . 107·941
- c.* Analysis of silver bromate and synthesis of silver bromide . . . 107·923
- d.* Analysis of silver iodate and synthesis of silver iodide . . . 107·937
- e.* Analysis of silver sulphate and synthesis of silver sulphide . . . 107·927

The mean value is  $\text{Ag} = 107·938$ , and its probable error is less than four units in the last place. This is a degree of accuracy which has scarcely been obtained elsewhere in the exact sciences, much less surpassed.

51. *Sodium*.—Berzelius (1811) determined the atomic weight of this metal, like that of potassium (p. 27), by conversion of the metal in sodium amalgam into sodium chloride. Penny (1839) found an almost absolutely correct value by the reduction of sodium chlorate to chloride. Pelouze (1845), Dumas (1859), and Stas determined the ratio between sodium chloride and silver; the results of the last give the best number at present known, viz.  $\text{Na} = 23·06$ .

52. *Strontium*.—We are indebted for our first knowledge of the atomic weight of this element to Stromeyer (1816), who analysed the carbonate and chloride. Pelouze (1845), Marignac (1858), and Dumas (1859) titrated strontium chloride with silver and obtained concordant results, viz.  $\text{Sr} = 87·5$ .

53. *Sulphur*.—The process by means of which Berzelius (1811) ascertained the atomic weight of sulphur for the first time, consisted in combining the same weight of lead first with oxygen, and then with sulphur; the number obtained was, to be sure, not very exact. He afterwards (1818) converted lead into lead sulphate, an experiment which Turner repeated (1833). Erdmann and Marchand (1844) analysed mercuric sulphide after fixing the atomic weight of mercury by analysis of the oxide (p. 25). Berzelius, who doubted their results, converted (1845) silver chloride into sulphide by heating in hydrogen sulphide. Struve (1851) decomposed silver sulphate by heating it in a current of hydrogen, when pure silver remains, and lastly, Dumas (1859) converted silver into silver sulphide by heating it in sulphur vapour.

The results of the majority of the experiments give values lying close to  $\text{S} = 32·0$ . It follows, however, from the more exact determinations of Stas (p. 17), that the true value is somewhat greater, viz.  $\text{S} = 32·06$ .

54. *Tantalum*. The atomic weight of this rare element is not even yet known with certainty. The older experiments of Rose, Berzelius, and Hermann gave quite untrustworthy results. The best numbers are got from the analyses of potassium tantalum fluoride by Marignac, and give  $\text{Ta} = 183$ .

55. *Tellurium*.—Berzelius (1812 and 1833) oxidised tellurium to dioxide. His numbers were nearly confirmed by those of Hauer (1857), who analysed potassium tellurium bromide. Wills (1879) repeated both experiments and got the same results.

In spite of this agreement the number obtained,  $\text{Te} = 128$ , must be considered improbable. For if we compare the following rows

P = 31·0	As = 75·0	Sb = 120·3
S = 32·1	Se = 79·1	Te = 128
Cl = 35·45	Br = 79·96	I = 126·86



we find in the three groups P, As, Sb ; S, Se, Te ; and Cl, Br, I, each of which comprises three similar elements, sulphur between phosphorus and chlorine, and selenium between arsenic and bromine ; but tellurium with the number 128 does not stand between antimony and iodine. Brauner (1883) found a source of error in the older determinations and obtained from the oxidation of tellurium to dioxide and from the formation of the sulphate  $\text{Te}_2\text{O}_4\text{SO}_3$  the atomic weight  $\text{Te} = 125$ , corresponding to analogy.

56. *Thallium*.—The first determinations by one of the two discoverers of thallium, Lamy (1862), from the analysis of the chloride and sulphate are not very exact. The results obtained by Werther (1864) from the analysis of thallium iodide, and by Hebbeling (1865) from the repetition of Lamy's experiments, are but little better. A research executed by the other discoverer, W. Crookes (1873), with all imaginable precautions, but unfortunately only according to one method (the conversion of the metal into the nitrate), gave  $\text{Tl} = 204.1$ .

57. *Thorium*.—Berzelius, who discovered this element, determined its atomic weight (1829) by analysis of the sulphate. The experiments were subsequently repeated by Chydenius (1863), Delafontaine (1863), Hermann (1864), and Cleve (1874), the analysis being mostly so conducted that thoria remained behind on strong ignition of the salt. Cleve analysed the oxalate in addition. Nilson, at first alone (1882), afterwards in conjunction with Krüss (1887), performed the analysis of the sulphate with material purified with especial care. Both researches yield the same number,  $\text{Th} = 232.4$ , which is somewhat lower than that found by the older investigators.

58. *Thulium*.—A still doubtful element, to which Cleve (1880) gives the atomic weight  $\text{Tu} = 171$  from analysis of the sulphate.

59. *Tin*.—The oxidation of the metal to dioxide has been almost exclusively employed for the determination of this atomic weight. We have such experiments by Berzelius (1812), Mulder and Vandeeren (1849), Vandeeren (1858), Dumas (1858), and van der Plaats (1885). In agreement with them are two analyses of the tetrachloride by Dumas. The mean value is  $\text{Sn} = 118.1$ .

60. *Titanium*.—The oldest determinations are due to H. Rose (1823 and 1829), and were obtained by roasting titanium sulphide to dioxide, and from the analysis of titanium chloride. The latter method has again been employed by Pierre (1847), Demoly (1849), and lastly by Thorpe (1883 and 1885), whose exact researches, which were also extended to titanium bromide, give  $\text{Ti} = 48.1$ .

61. *Tungsten*.—The atomic weight of tungsten has been usually determined from the reduction of the trioxide to metal, and from the oxidation of the metal to trioxide,—Berzelius (1825), Schneider (1850), Borch and Dumas (1859). Roscoe (1872) from an analysis of the hexachloride obtained the same result. Other determinations, such as the analysis of barium metatungstate by Scheibler (1861) and of ferrous tungstate by Zettnow (1867), are of less importance. The mean of the good determinations is  $\text{W} = 184.0$ .

62. *Uranium*.—Up to the year 1840 the atomic weight of uranium had been calculated quite erroneously from the experiments of Arfvedson (1825) and Berzelius (1825), for the black product  $\text{UO}_2$  got by the reduction of

the higher oxides was looked upon as metallic uranium until Péligot showed that it contained oxygen. He at the same time determined the atomic weight pretty accurately from analysis of uranyl acetate. Later researches by Ebelmen (1842) and Wertheim (1843) are of little importance, but the very careful work of Cl. Zimmermann (1882 and 1886) deserves great attention. The methods employed were not in themselves particularly good, but excellent results were obtained by scrupulous care being used in the performance of the experiments. One series consisted in the reduction of  $U_3O_8$  to  $UO_2$  in a current of hydrogen, the other in the conversion of sodium uranyl acetate,  $Na(UO_2)(C_2H_3O_2)_3$ , into sodium diuranate,  $Na_2U_2O_7$ , by roasting. The mean value is  $U = 239.4$ . It may be mentioned that uranium has the highest atomic weight of all the elements.

63. *Vanadium*.—An error similar to that in the case of uranium was also committed with this metal. It was only found out in 1868 by Roscoe, who showed that the substance formerly held to be the metal was really an oxide  $VO$ . If we take this into account in calculating the analyses of vanadic acid and of vanadyl chloride by Berzelius (1831), we arrive at pretty correct numbers. Our present accurate knowledge of the atomic weight of this element is due to an excessively careful investigation by Roscoe (1868), who reduced vanadic acid to oxide in a current of hydrogen, and also titrated vanadyl chloride with silver. The mean of the two series is  $V = 51.2$

64. *Ytterbium*.—Marignac in 1872 discovered in the substance regarded up till that time as erbia a perfectly colourless earth with no absorption spectrum, to which he gave the name of ytterbia. Immediately thereafter Delafontaine found the same substance in allanite from Amherst, and Nilson, too, soon confirmed the existence of the new element. Its atomic weight was found pretty concordantly to be  $Yb = 173.2$ .

65. *Yttrium*.—This element also was only gradually distinguished and separated from the earths which always accompany it, and we cannot even yet state with certainty that what is known as yttrium is really a chemical species. Delafontaine (1865) was probably the first to work with tolerably pure material. The method he adopted was the conversion of the earth into sulphate, and this was also done by Bahr and Bunsen (1866), Cleve and Höglund (1873), and Cleve (1873). The mean of the better determinations is  $Y = 88.7$ .

66. *Zinc*.—Even the oldest researches by Berzelius (1811) yielded a result very near the truth. His method was the conversion of the metal into oxide. The number obtained was called in question on quite insufficient grounds by Jacquelin in 1842, and shortly thereafter Favre sought by the analysis of zinc oxalate, as well as by dissolving zinc in sulphuric acid and burning the evolved hydrogen to water, to show the correctness of a higher value. Berzelius caused A. Erdmann (1843) to undertake new oxidation experiments, which approximately confirmed his previous numbers. Still nearer Berzelius's value are the numbers lately found by Marignac from the analysis of potassium zinc chloride. Baubigny (1883) by analysis of the sulphate, van der Plaats (1885) by solution of zinc in sulphuric acid and measurement of the hydrogen evolved, and lastly Ramsay and Reynolds (1887), by the same methods have found similar values. The mean of all the determinations is  $Zn = 65.5$ .

67. *Zirconium*.—The atomic weight of this element has been only twice determined: once by Berzelius (1825) from the analysis of the sulphate, and once by Marignac (1860) from the analysis of potassium zirconium fluoride. The latter obtained  $Zr = 90.7$ .

In the following table the atomic weights of the elements at present known are collected; O = 16 is taken as the basis of the calculation, hydrogen being thus H = 1.003—

1. Aluminium	Al = 27.08	31. Molybdenum	Mo = 95.9
2. Antimony	Sb = 120.3	35. Nickel	Ni = 59 (?)
3. Arsenic	As = 75.0	36. Niobium	Nb = 94.2
4. Barium	Ba = 137.0	37. Nitrogen	N = 14.011
5. Beryllium	Be = 9.10	38. Osmium	Os = 192
6. Bismuth	Bi = 208.0	39. Palladium	Pd = 106
7. Boron	B = 11.01	40. Phosphorus	P = 31.03
8. Bromine	Br = 79.963	41. Platinum	Pt = 194.8
9. Cadmium	Cd = 112.1	42. Potassium	K = 39.14
10. Cesium	Cs = 132.9	43. Rhodium	Rh = 103
11. Calcium	Ca = 40.0	44. Rubidium	Rb = 85.4
12. Carbon	C = 12.0	45. Ruthenium	Ru = 101.7
13. Cerium	Ce = 140.2	46. Samarium	Sm = 150
14. Chlorine	Cl = 35.453	47. Scandium	Sc = 44.1
15. Chromium	Cr = 52.2	48. Selenium	Se = 79.1
16. Cobalt	Co = 59 (?)	49. Silicon	Si = 28.4
17. Copper	Cu = 63.3	50. Silver	Ag = 107.938
18. Didymium	{ Nd = 140.8 Pr = 143.6	51. Sodium	Na = 23.06
19. Erbium	Er = 166	52. Strontium	Sr = 87.5
20. Fluorine	F = 19.0	53. Sulphur	S = 32.06
21. Gallium	Ga = 69.9	54. Tantalum	Ta = 183
22. Germanium	Ge = 72.3	55. Tellurium	Te = 125
23. Gold	Au = 197.2	56. Thallium	Tl = 204.1
24. Indium	In = 113.7	57. Thorium	Th = 232.4
25. Iodine	I = 126.86	58. Thulium	Tu = 171
26. Iridium	Ir = 193.2	59. Tin	Sn = 118.1
27. Iron	Fe = 56.0	60. Titanium	Ti = 48.1
28. Lanthanum	La = 138.5	61. Tungsten	W = 184.0
29. Lead	Pb = 206.91	62. Uranium	U = 239.4
30. Lithium	Li = 7.03	63. Vanadium	V = 51.2
31. Magnesium	Mg = 24.38	64. Ytterbium	Yb = 173.2
32. Manganese	Mn = 55.0	65. Yttrium	Y = 88.7
33. Mercury	Hg = 200.4	66. Zinc	Zn = 65.5
		67. Zirconium	Zr = 90.7

## CHAPTER IV

### NUMERICAL RELATIONS OF THE ATOMIC WEIGHTS

Two directions have been taken in the attempts to draw general conclusions from the material offered by the atomic weights of the elements. A line of thought first pursued by Prout (1815) and shortly afterwards by Meinecke (1817) starts from the philosophical assumption of a fundamental substance or "protyle." This was thought to exist in hydrogen, and therefore the conclusion had to be drawn that, if all the other elements consisted of hydrogen, their atomic weights must be multiples of that of hydrogen.

This hypothesis was widely diffused in England, especially through the instrumentality of Thomas Thomson, the author of a then popular treatise on chemistry, who sought to support it by experiments, which were, however, very insufficient for the purpose. On the Continent it met with no success, as Berzelius had declared it to be incorrect from the consideration of his own determinations; and the review of the whole question by Turner at the instigation of the British Association proved the accuracy of Berzelius's numbers.

However, when the error in the atomic weight of carbon was discovered in 1842, and this was shown by the work of Dumas and Stas to be to that of hydrogen as nearly as possible in the ratio 12 : 1, and when, in addition, Dumas found the atomic weights of oxygen and nitrogen to be respectively sixteen and fourteen times that of hydrogen, the French savant did not delay in expressing his conviction that a general law was here in question. He devoted himself afterwards to test this, and came to the conclusion that though all the atomic weights were not multiples of that of hydrogen, still the half of this value was the basis of all the others. He was afterwards forced, however, to halve this unit also, so that according to his latest views all the atomic weights might be represented as multiples of the fourth part of that of hydrogen.

The whole subject loses the greater part of its interest by this qualification, as the degree of accuracy of the determinations in the

case of many elements does not reach the unit given by Dumas, so that the hypothesis cannot really be tested.

The same question was taken up simultaneously by J. S. Stas, who restricted himself to the investigation of fewer elements than Dumas, but far surpassed his teacher and former collaborator in the exactness of his determinations, an exactness never reattained. Stas gives as the result of his researches the opinion that Prout's hypothesis is altogether inadmissible; it represents merely an approximation to the truth, all the atomic weights determined by him differing from those required by the hypothesis by quantities much larger than the possible errors of experiment can account for.

Although the question seemed finally settled by this unsurpassed work, it has nevertheless always sprung up again. The reason of this is the real approximation, already mentioned, of the values to multiples of the atomic weight of hydrogen. A glance at the table on p. 32 shows this plainly. There have consequently always been people who considered the integral values to be the only correct ones. No explanation at all probable of the actual deviations has yet been given; especially so, as no chemical process is known in which the mass of the given material undergoes any change. We must therefore at present simply take the numbers as experiment gives them, and leave unanswered the question as to the cause of their surprising approximation to multiples of hydrogen.

Besides these considerations, hitherto fruitless, another series on the same subject but in the opposite direction has been pursued from the beginning. This series, in contrast to the former, has yielded well-defined regularities, which are submitted to the reader in the following pages.

J. B. Richter (1798), after his first discoveries on the mass relations exhibited when an acid is neutralised by different bases—the beginning of the scientific investigation of the subject,—at once conceived the idea that his constants, quite apart from their general significance, were subject to special laws. If they were arranged according to their magnitude, the numbers in his opinion followed a strict law, for which he assumed different expressions at different times. The general acceptance of the fundamental law discovered by Richter was much retarded by his holding to the above idea with such tenacity that he almost lost sight of the chief discovery. However, he was so far justified in that the regularities suspected by him actually exist, although not in the form he attributed to them.

At first only the constant combining numbers for acids and bases, and afterwards those for metals, received the above-mentioned generalisation, a generalisation which led to the atomic theory. Soon after the advancement of this theory, Döbereiner (1817) drew attention to a certain regularity by showing that the atomic weight of strontium (87.5) lay midway between the atomic weight of calcium (40.0) and

that of barium (137.0). For our more exact numbers, which I have placed in brackets, this is not strictly true, as the calculated value is 88.5 instead of 87.5, but the approximation is at all events remarkable, especially as we find the same thing several times repeated. Lenssen (1857), indeed, attempted to arrange all the elements in triads in this way.

Pettenkofer's supposition (1850), that the atomic weights of similar elements form arithmetical series, is more like the original ideas of Richter again. Kremers, Gladstone, and especially Dumas, further developed the subject in various ways.

The idea which proved to be the most fruitful was enounced by Newlands in 1864, although in somewhat inadequate form, so that it did not find ready recognition. He not only arranged the similar elements in series, but also the whole of the elements according to the magnitude of their atomic weights. It appeared from this arrangement that similar elements were found at approximately equal distances in the series; counting from any one element, every eighth was in general more similar to the first than the other elements. This he called the Law of Octaves, but did not succeed in fully carrying it out.

Lothar Meyer and Mendelejeff independently (1869) met with more success, and their conclusion may be expressed as follows: the properties of the elements are periodic functions of their atomic weights. Thus, if all the elements are arranged in the order of their atomic weights in a series, their properties will so vary from member to member that after a definite number of elements have been passed either the first or very similar properties will recur.

The carrying through of this idea met with great difficulties at the outset. The reason lay partly in the fact that at that time there was no systematic way of choosing the true atomic weight from those that appeared probable. For instance, if it is determined that carbon combines with oxygen in the ratios 12:16 and 12:32, it is, without other information, quite arbitrary to assume in the first compound one atom of carbon to one atom of oxygen, and in the second, one atom of carbon to two atoms of oxygen. We might just as well put the atomic weight of carbon equal to 6 and write the compounds  $C_2O$  and  $CO$ , or equal to 24, when the formulæ would become  $CO_2$  and  $CO_4$ . The sides from which this problem of the right choice of the atomic weights could be attacked were manifold, as will be seen later, but at the period when Meyer and Mendelejeff developed their views there was no agreement as to how the attack ought to be made, in fact the principle we are discussing had often to be applied to decide between the possible values.

Besides this difficulty another had to be overcome, namely, that which lay in the actual false determination of some equivalents. Here, however, it was generally merely a question of transposing two neighbouring elements, several instances of which have been already mentioned (*e.g.* p. 29), a more

correct determination being brought about by this circumstance. Mendelejeff was both most energetic and most successful in this respect.

The following is the table of the elements given by Lothar Meyer—

I	II	III	IV	V	VI	VII	VIII
Li	Be	B	C	N	O	F	—
Na	Mg	Al	Si	P	S	Cl	—
K	Ca	Sc	Ti	V	Cr	Mn	Fe, Co, Ni
Cu	Zn	Ga	Ge	As	Se	Br	—
Rb	Sr	Y	Zr	Nb	Mo	—	Ru, Rh, Pd
Ag	Cd	In	Sn	Sb	Te	I	—
Cs	Ba	La, Di, Ce	—	—	—	—	—
—	—	Yb	—	—	—	—	—
—	—	—	—	Ta	W	—	Os, Ir, Pt
Au	Hg	Tl	Pb	Bi	—	—	—
—	—	—	Th	—	U	—	—

The elements are so arranged in this table that the atomic weights follow in order from left to right, the first of the second line following immediately after the last of the first line, and so on.

Mendelejeff prefers another arrangement. In his table, given below, the values increase from above downwards. It differs from Meyer's table, in addition to the rotation through a right angle, by being ordered in fifteen rows instead of eight, which renders the relations somewhat more plain.

R <sub>2</sub> O I	Li	K	Rb	Cs	—	—
RO II	Be	Ca	Sr	Ba	—	—
R <sub>2</sub> O <sub>3</sub> III	B	Sc	Y	La	Yb	—
RO <sub>2</sub> IV	C	Ti	Zr	Ce	—	Th
R <sub>2</sub> O <sub>5</sub> V (III)	N	V	Nb	Di	Ta	—
RO <sub>3</sub> VI (II)	O	Cr	Mo	—	W	U
R <sub>2</sub> O <sub>7</sub> VII (I)	F	Mn	—	—	—	—
VIII	—	{ Fe Co Ni	{ Ru Rh Pd		{ Os Ir Pt	
R <sub>2</sub> O I	Na	Cu	Ag	—	Au	—
RO II	Mg	Zn	Cd	—	Hg	—
R <sub>2</sub> O <sub>3</sub> III	Al	Ga	In	—	Tl	—
RO <sub>2</sub> IV	Si	Ge	Sn	—	Pb	—
R <sub>2</sub> O <sub>5</sub> V (III)	P	As	Sb	—	Bi	—
RO <sub>3</sub> VI (II)	S	Se	Te	—	—	—
R <sub>2</sub> O <sub>7</sub> VII (I)	Cl	Br	I	—	—	—

The content of the two tables is the same; the corresponding elements of the different sections are similar to each other—the perpendicular columns of Meyer's table and the horizontal rows of Mendelejeff's. From the former we see that the periodicity of properties is a double one, every member having the greatest similarity, not to

the next member, but to the next but one. Mendelejeff has, therefore, separated these two groups by doubling the number of rows.

The analogies are most marked in the general chemical properties, especially in the capability of forming acids or bases. Taking Mendelejeff's table, we have in the first row the very strongly basic alkali metals, the likewise strongly basic metals of the alkaline earths in the second row; then follow the metals of the earths whose oxides are weakly basic; next come the elements of the carbon group, the oxides of which are partly weak acids; the acid properties in each row diminishing with increasing atomic weight. The members of the sixth row are already decidedly acid-forming, and those of the seventh exhibit this property in the most marked manner.

The same order is repeated in the lower portion of the table. The intermediate elements of the iron and platinum groups are not easy to dispose of; they are mostly distinguished by a pronounced tendency to form several different series of compounds.

A very remarkable regularity is observed with respect to the valency of the elements, as is indicated by the Roman numerals in Mendelejeff's table. This property increases from 1 to 4; from this point on the elements have mostly more than one valency, one towards chlorine, oxygen, etc., which increases as we proceed, and one towards hydrogen, which decreases at the same rate.

Further regularities shown by the physical properties of the elements as well as of their compounds in the preceding arrangement will be discussed later.

In both tables there are many vacant places. They belong to elements not yet discovered. Mendelejeff made use of the regularities just mentioned to predict the properties of unknown elements from those of their neighbours in the table. He gave especially a somewhat detailed description of scandium, gallium, germanium, and their compounds, none of which were known at the time he wrote his memoir, and to him as well as to science in general has been accorded the triumph of seeing these predictions for the most part fulfilled on the subsequent discovery of the elements.

The "periodic system" of the elements is by no means perfect. Elements are frequently parted in the preceding tables, which an unprejudiced observer would consider analogous in their compounds (*e.g.* copper and mercury), while others are placed together which appear altogether dissimilar, as sodium with copper, silver, and gold. It is to be hoped that such incongruities will be removed in the future by new facts and by fresh considerations. The periodic system is therefore not to be looked upon as the conclusion, but rather as the commencement of a train of ideas eminently fruitful.

We may conclude this book by an observation of a general character. From the fact that the mass of the various substances is not changed in a chemical process, it is apparent that the mass of a chemical com-



pound is the sum of the masses of its components. Such properties, which are independent of the state of chemical combination, and whose numerical value in compounds therefore appears as the sum of the values belonging to the different components, will in future be called additive. From the existence of such properties it has been concluded that chemical compounds actually contain their components as such, the order only being changed; the additive properties form therefore the foundation of the atomic theory.

## BOOK II

### THE PROPERTIES OF GASES

#### CHAPTER I

##### GENERAL PROPERTIES

MATTER in the gaseous state is distinguished by its capability of completely filling any given space as well as by its want of any definite form. In this state matter occupies more space than in any other, and obeys simpler laws.

A given mass of gas occupies a definite volume  $v$  only when it is at a definite temperature  $t$  and under a definite pressure  $p$ . In general we may put  $v = f(p, t)$ , where  $f(p, t)$  signifies a function of  $p$  and  $t$  whose form is to be determined.

The influence of pressure is such that when the pressure increases the volume diminishes in the inverse ratio. This law was discovered by Robert Boyle (1662) and goes at present mostly under his name. On the Continent it was usually called until recently Mariotte's Law, but this physicist published it only in 1679. The algebraic expression of the law is

$$v : v' = p' : p,$$

or

$$vp = v'p',$$

where  $v$  and  $p$ ,  $v'$  and  $p'$  are two pairs of corresponding volumes and pressures which one and the same gas occupies at the same temperature. That is, at a given temperature the product of the pressure and volume of a quantity of gas remains constant.

This law holds for all gases, no matter what their chemical nature, from which we may conclude that the cause of the law is to be found in something which is likewise independent of the chemical nature of the gas.

A similar independence is found in the influence of temperature

on the volume of gases. The law which obtains here was discovered simultaneously (1802) by Gay-Lussac and Dalton, and is usually named after the former.\* According to this law all gases expand in the same proportion for the same increase of temperature.

If we put the volume of a gas at the temperature of melting ice and under a definite pressure equal to unity, it will be 1.367 when the temperature rises to that of boiling water. This range of temperature is usually divided into 100 parts, which are so determined that for every part the same increase of volume (namely .00367) occurs, and these grades of temperature are called centigrade degrees. They are reckoned from the melting-point of ice, upwards with the positive and downwards with the negative sign. The increase of volume per degree is according to definition for all gases the same, and amounts to .00367 or  $\frac{1}{273}$  of the volume at  $0^{\circ}$ ; it is called the coefficient of expansion.

The algebraic expression for this relation is found in the following formula—

$$v = v_0(1 + at),$$

where  $v$  is the volume at the temperature  $t^{\circ}$ ,  $v_0$  that at  $0^{\circ}$ ;  $a$  is the coefficient of expansion.

If we warm the gas without allowing it to expand, the pressure increases. This increase may be easily calculated from Boyle's Law. Suppose the gas by heating to have expanded from  $v_0$  to  $v$ , and afterwards to be compressed again to  $v_0$  at the temperature  $t$ , then according to Boyle's Law the pressure  $p_0$  at  $0^{\circ}$  must be to the pressure  $p$  at  $t^{\circ}$  inversely as the corresponding volumes, *i.e.*

$$p_0 : p = v_0 : v,$$

or

$$pv_0 = p_0v.$$

If this equation is combined with the former, we have

$$p = p_0(1 + at).$$

Thus at constant volume the pressure increases with the temperature in the same measure as the volume does under constant pressure. The relative increase of pressure per degree, or the coefficient of tension, is consequently equal to the coefficient of expansion.

Lastly, if we allow both pressure and volume to change, their product, which at constant temperature is constant, varies with varying temperature in the same way as each of the factors would do separately if the other were constant. For this general case we have, therefore,

$$pv = p_0v_0(1 + at).$$

This equation permits of the calculation of the volume which a gas would occupy at normal temperature and pressure when we know its

\* In England it is also frequently called Charles's Law.—(Tr.)

volume at any given temperature  $t$  and pressure  $p$ . The standard values have been conventionally fixed so that the normal temperature is that of melting ice, or zero centigrade, and the normal pressure that of a column of mercury 76 cm. high, equal to a weight of 1033 g. per sq. cm.\* For this purpose the equation is written in the form

$$v_0 = \frac{pv}{p_0(1 + at)},$$

which is frequently employed in practice.

We can give the general equation  $p v = p_0 v_0 (1 + at)$  a simpler form by making use of the following consideration. Since a gas expands  $\cdot 00367$  or  $\frac{1}{273}$  of its volume at  $0^\circ$  for every degree above  $0^\circ$ , it must at  $273^\circ$  have its original volume doubled. On the other hand if we cool the gas below  $0^\circ$ , in the same way the volume decreases for every degree by  $\frac{1}{273}$  of its volume at  $0^\circ$ , and is therefore reduced to zero at  $-273^\circ$ . It is as a matter of fact impossible to reach the temperature of  $-273^\circ$ , and that the law of expansion for gases is valid to this point is open to doubt. Hypothetically, however, we can look upon the law as holding as far down as  $-273^\circ$ , so that we may take this temperature as the zero of a new scale in which every temperature has a numerical value greater by 273 than it has in the centigrade scale. If we call these new temperatures absolute temperatures and denote them by  $T$ , then according to definition,  $T = t + 273$ , or  $t = T - 273$ . If for  $t$  in the equation  $p v = p_0 v_0 (1 + at)$  we substitute  $T - 273$ , we obtain  $p v = p_0 v_0 \left( 1 + \frac{T - 273}{273} \right)$  since  $a = \frac{1}{273}$ , or  $p v = \frac{p_0 v_0}{273} T$ . If finally

the constant  $\frac{p_0 v_0}{273}$  is made equal to  $R$ , we obtain the following simple expression

$$p v = R T,$$

*i.e.* the product of the volume and pressure of a gas is proportional to its absolute temperature.

These laws of gases do not rank in respect of accuracy along with the fundamental laws of Book I. While the latter have stood every test, and must in our present state of knowledge be looked upon as absolutely exact, it is entirely otherwise with those we are now considering. These must be looked upon as ideal limiting cases, to which the behaviour of existing gases approximates more or less closely, without ever actually attaining them.

The first investigations on this subject were made by Despretz in 1825, though some isolated observations had already been communicated by van Marum and Oersted. He came to the conclusion that gases which are near

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\* Mercury is 13.595 times heavier than water; a column 1 sq. cm. in section and 76 cm. high contains 76 c. cm., and (as 1 c. cm. water weighs 1 g.) weighs therefore  $76 \times 13.595 = 1033$  g.

the point where they pass into liquids are more compressible than they ought to be according to Boyle's Law.

Arago and Dulong, who in 1829 took up the experiments with greater experimental means at their disposal, could discover no deviation in the case of air up to 27 atmospheres. Other gases were not investigated. Pouillet compared carbon dioxide, nitrogen monoxide, methane, and ethylene with air, and found with all these gases deviations in the same sense, namely that they were more compressible than corresponded to Boyle's Law. The last two gases were not then known in the liquid state. Very comprehensive experiments were afterwards carried out by Regnault. It resulted from them that no gas was found to obey Boyle's Law exactly. Besides the already known deviation of too great compressibility, hydrogen showed the opposite behaviour—was according to Regnault a "*gaz plus que parfait*."

However, it soon appeared that this, at first quite unexpected, behaviour is shown by all gases under very high pressures, provided they do not liquefy under the pressure. Natterer discovered this in the course of his attempts to liquefy the so-called permanent gases, oxygen, hydrogen, and air.

The anomaly observed by Regnault in the case of hydrogen is therefore no peculiarity of this gas, but is exhibited by all gases, only at different pressures.

Interesting and inviting to further research as Natterer's results were, nearly twenty years passed before a more thorough investigation of the subject was begun. In 1870 Cailletet, and simultaneously Amagat, again took up the matter. The latter especially has greatly advanced our knowledge of the question.

The following diagrams (Figs. 1-5) give a representation of Amagat's results. The pressures are plotted on the horizontal axes; on the vertical axes we have the values of the product  $p_v$ . If the gases followed Boyle's Law exactly,  $p_v$  would be constant and the curve would become a straight line parallel to the horizontal axis. As we see, no gas corresponds to this simple case. Most of them exhibit a decrease of the product at low pressures, *i.e.* they are then more compressible. At high pressures, on the other hand, the product  $p_v$  is without exception greater, and all the gases behave like hydrogen.

This points to the deviations of gases from the simple law being conditioned by two circumstances, one of which causes the decrease at low pressures, the other the increase at high pressures. Later we shall see what conception of the cause of such behaviour may be made from the standpoint of the molecular theory.

The investigations made with respect to the behaviour of gases at low pressures have yielded no concordant results. It seems probable, however, that the view according to which all gases approximate with diminishing pressure more and more to the ideal gaseous state, *i.e.* to strict obedience to Boyle's Law, is the correct one.

The deviation of gases from the simple laws takes place not only when the pressure but also when the temperature varies. At first the coefficient of expansion was determined by Gay-Lussac as well as by Dalton considerably too high. After the correction of the value by Rudberg, Magnus investigated several gases and found marked differences amongst them. As in the other

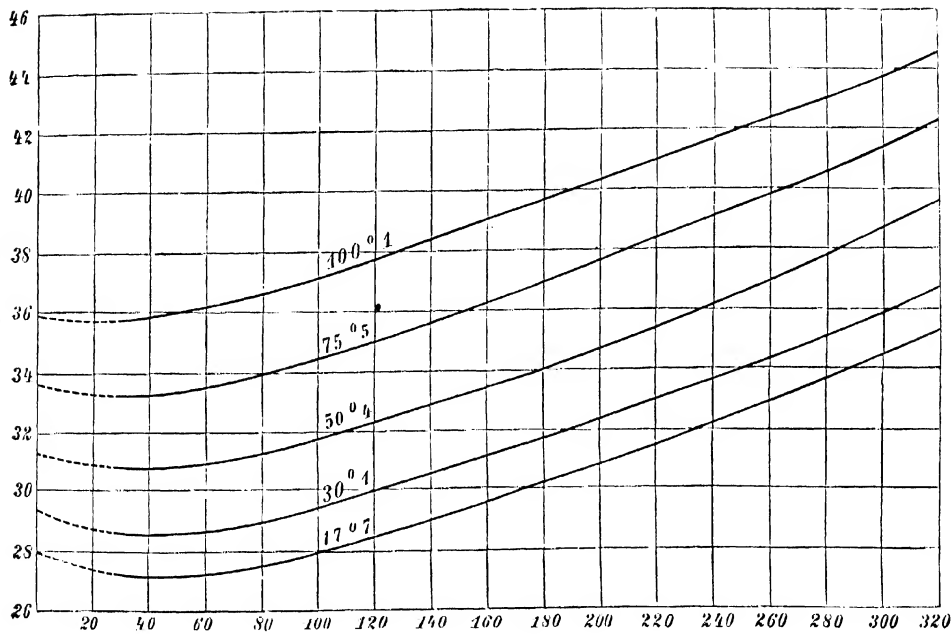


FIG. 1. NITROGEN.

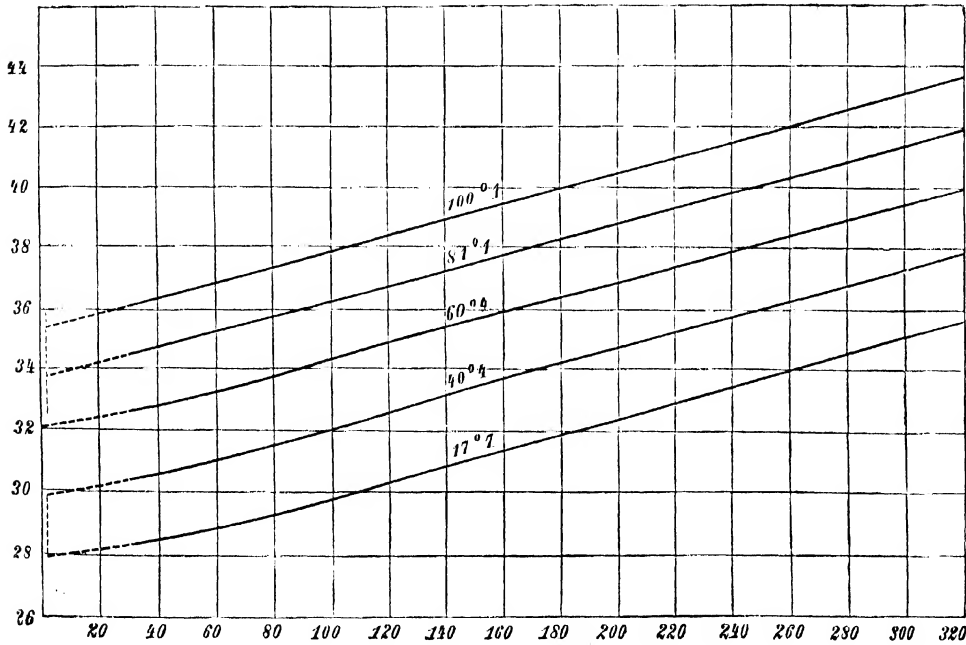


FIG. 2. HYDROGEN.

case, the deviations are greatest with the gases that are nearest their point of condensation, and the coefficients of such gases are greater than those of

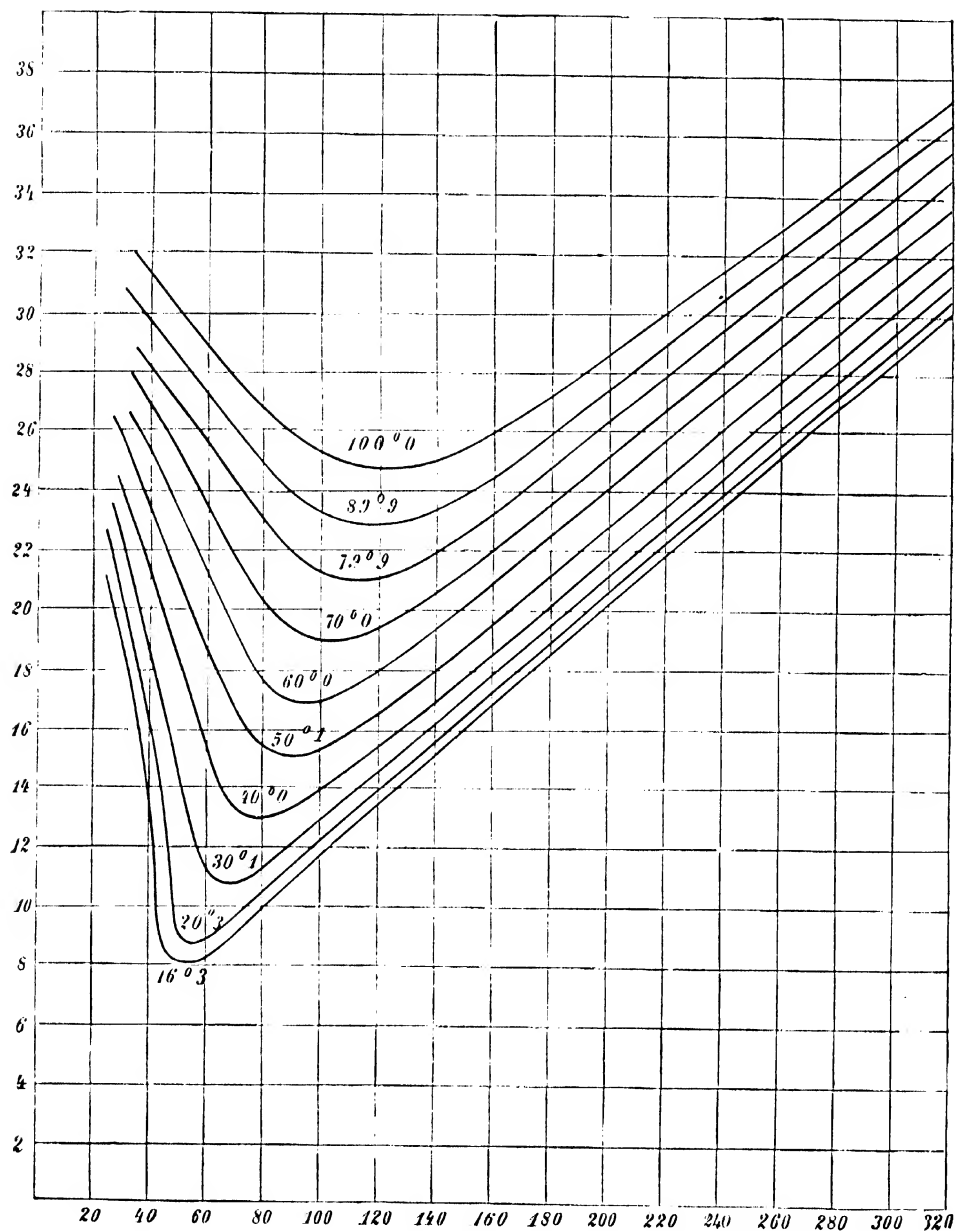


FIG. 3. ETHYLENE.

normal gases. These deviations are such that they become smaller as the temperature increases.

As already mentioned, the divergence from the laws is very great when the gases are near their point of condensation. It is naturally still greater

when the substances in question are liquid at ordinary temperatures and only at relatively high temperatures assume the gaseous form. All bodies, however, do not behave alike in this respect, for while for most substances the varia-

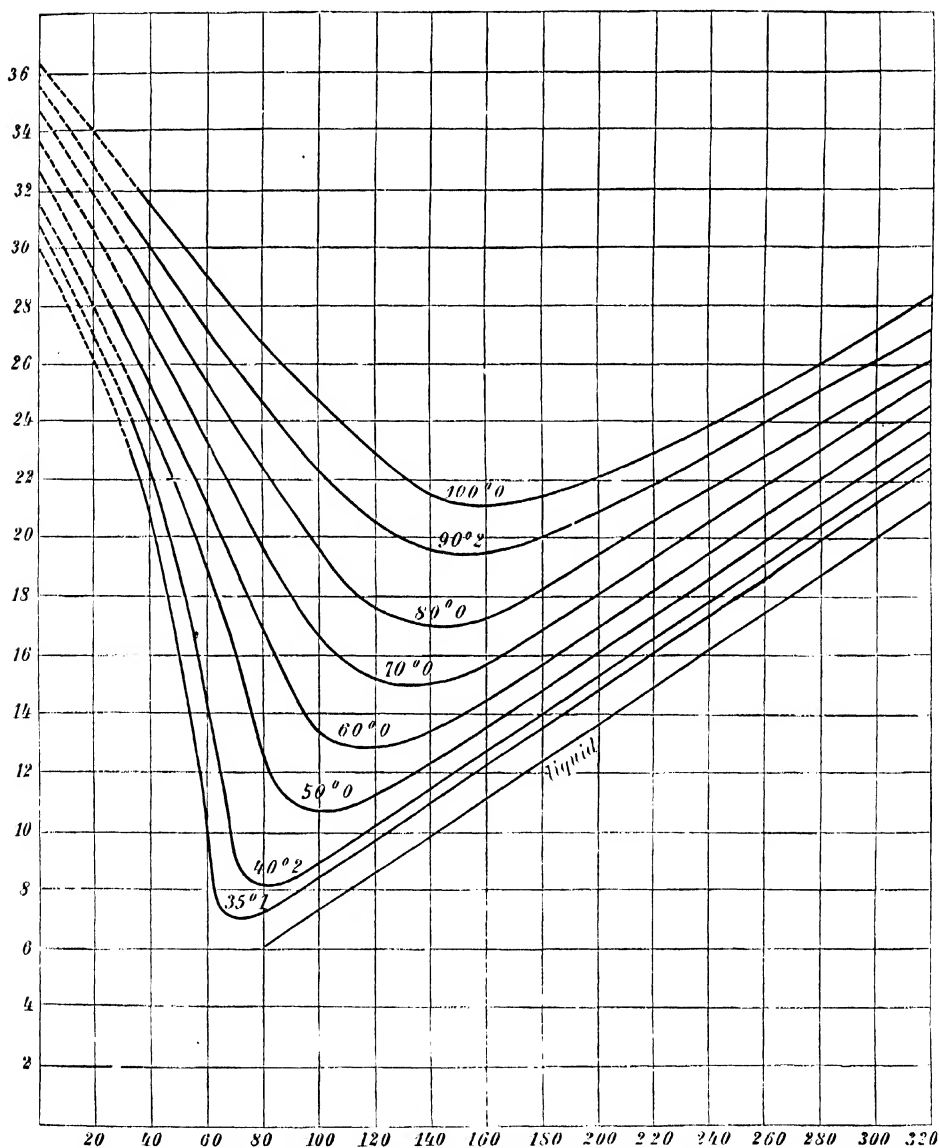


FIG. 4. CARBON DIOXIDE.

tions remain within comparatively narrow limits, for some others they are exceedingly large. In such cases we have every ground to assume special circumstances conditioned by the chemical nature of the substances. Acetic acid in particular has proved to be such an exceptional case, its density varying greatly with pressure and temperature when compared to that of



normal gases under the same conditions. Only when a very high temperature is reached does gaseous acetic acid behave like a normal gas.

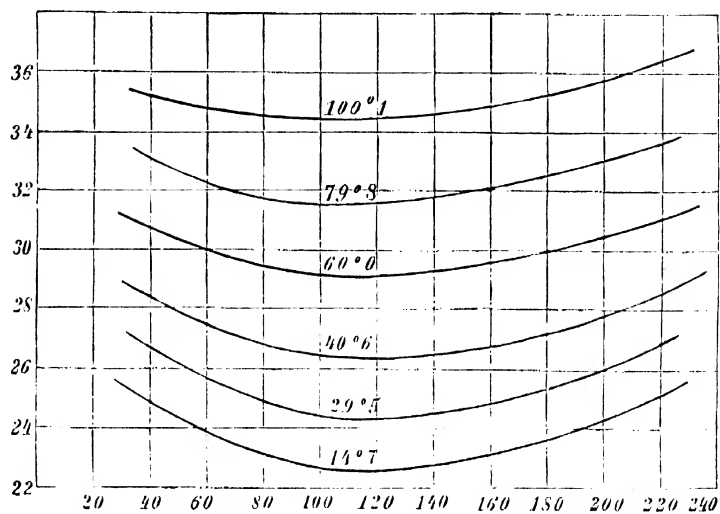


FIG. 5. METHANE.

## CHAPTER II

### SPECIFIC GRAVITY AND VOLUME OF GASES

If equal volumes of different gases at the same temperature and pressure be exposed to any (equal) alterations in these conditions, the volumes in consequence of the above laws will always remain equal to each other. The masses and weights of equal volumes of different gases will therefore always be in the same ratio if both have the same temperature and pressure, no matter what values these may assume.

On this circumstance is based the conception of the specific gravity of gases, which is the ratio of the weights of equal volumes of the gas in question and of a standard gas measured under the same conditions.

In physics, atmospheric air is usually taken as the standard gas. This choice, however, is rather unfortunate, since the composition of the air, which is merely a mixture, is not constant, and therefore the weight of the same volume of air exhibits corresponding variations.

It answers the chemist's purpose much better to use a pure gas for the standard. Oxygen has most to be said in its favour, as it also serves as the standard element in the determination of atomic weights.

The weight of a cubic centimetre of oxygen is, according to the exact measurements of Regnault,  $\cdot 001430$  g. at  $0^{\circ}$  and 76 cm. This weight varies with temperature and pressure, thus

$$W = \cdot 001430 \frac{p}{76(1 + at)},$$

where the pressure  $p$  is expressed in centimetres of mercury and the temperature  $t$  in centigrade degrees;  $a$  is the coefficient of expansion  $\cdot 00367$ . The weight of  $v$  c. cm. of oxygen has the value  $Wv$ .

For many calculations it is of importance to know the volume of one gram of oxygen. This (*i.e.* the specific volume of oxygen) is at  $0^{\circ}$  and 76 cm. equal to  $\frac{1}{\cdot 001430}$ , or 699.4 c. cm., and varies according to the formula

$$\phi = 699.4 \frac{76(1 + at)}{p}.$$

Lastly, we shall often make use of the volume of 32 g. of oxygen (equal to double the atomic weight in grams). This comes to

$$22381 \frac{76(1 + at)}{p} \text{ c. cm.}$$

To enable the student to calculate with the old data which have the specific gravity of air as unit, it may be mentioned that 1 c. cm. of air of the ordinary composition weighs .001293 g., and that its specific volume is 773.3 c. cm. at normal temperature and pressure. For other temperatures and pressures the same factors as for oxygen are used.

The knowledge of the specific gravities of different gases has a special interest for the chemist, and different methods have, therefore, been contrived to arrive at it. These all come in the end to the same thing, viz. both the volume and the weight of a given quantity of gas are determined at a definite temperature and pressure. If we then calculate how much an equal volume of the standard gas weighs under the same conditions, the ratio of the two weights gives the specific gravity required. If  $W$  is the weight of  $V$  volumes of the gas to be investigated at the temperature  $t$  and the pressure  $p$ , that of an equal volume of air is

$$w = .001293 \frac{pV}{76(1 + .00367t)},$$

and the specific gravity required,  $d = \frac{W}{w}$ , has the value

$$d = \frac{W76(1 + .00367t)}{.001293pV} = \frac{W(1 + .00367t)}{.0000170pV}.$$

This equation holds for all methods of determining vapour densities; its application presupposes that the pressures are measured in centimetres of mercury, the volumes in cubic centimetres, the weights in grams, and the temperatures in centigrade degrees. The various methods differ only in the means adopted to get a knowledge of these four requisite numbers.

If it is required to get as accurate determinations as possible of the density of gases that can be investigated at comparatively low temperatures, two equal glass globes of suitable size are employed; these can be closed by means of stop-cocks, and are exactly equalised as regards their weight and external volume. One of the globes is closed (preferably when exhausted) and this then serves as a counterpoise to the other, which is weighed alternately empty and filled with the gas whose density is to be determined. The counterpoise of equal external volume is rendered necessary by the fact that the total upward pressure exercised on the globes by the air in which they are weighed is about as great as the weight of the gas itself, and that this pressure is variable with the condition of the atmosphere. If,

however, the variations affect both sides of the balance equally, as they do in the arrangement described, they have no influence on the result of the weighing. When the globe is weighed exhausted of air its volume is rendered somewhat smaller by the external atmospheric pressure, and consequently the upward pressure is also smaller, so that in very exact measurements this circumstance must be taken into account.

The difficulties encountered in such experiments lie in the necessity of weighing the large gas receptacles with great accuracy; the determination of the pressure, volume, and temperature can be made with sufficient exactness much more easily. In consequence of this we may frequently attain the desired end more conveniently and with greater precision by weighing the gas, not as a gas, but in the solid or liquid state. This by no means presupposes that the gas as such may be easily brought into this state; we can make use of this mode of procedure whenever the gas can be generated from solid or liquid compounds, or can be converted into these. For example, to find the specific gravity of oxygen, Buff weighed a retort filled with potassium chlorate, generated oxygen from this, measured the volume, pressure, and temperature of the gas, and weighed the retort a second time. The difference between the two weights gives the weight of the oxygen measured. Conversely, Marchand led the still unknown quantity of oxygen, whose volume, pressure, and temperature he had determined, by the aid of an indifferent gas (carbon dioxide), over a weighed quantity of red-hot copper, which united with the oxygen to form copper oxide, so that from the increase in weight he obtained the weight of the oxygen. It is easy to see how these methods may be applied in other cases.

When great accuracy is not required, or when only small quantities of gas are at our disposal, the scale of the experiments is considerably lessened. Very often the chemist has to determine the specific gravity of gases that at ordinary temperatures possess the solid or liquid form—of vapours. To this end smaller bulbs of from 200 to 500 c. cm. capacity are used, into which some of the substance is introduced. By exposing the bulbs to a temperature considerably ( $30^{\circ}$  to  $50^{\circ}$  at least) above the boiling-point of the substance, so that a rapid evolution of gas is brought about, we can displace all the air contained in the bulb by the vapour. When the stream of vapour ceases to issue from the drawn-out neck of the bulb, this is sealed off and the temperature and barometric pressure observed. The weight is found from the difference in weight of the bulb when empty and when filled with vapour (the upward pressure being taken into account), and the volume is obtained by weighing the bulb empty and filled with water at  $4^{\circ}$ ; the difference of weight in grams is equal to the capacity in cubic centimetres. It must not be forgotten that the bulb at the temperature of observation has a somewhat larger volume, because it is expanded by the heat; the increase for glass, about 00003 per degree, is not inconsiderable. (Dumas.)

We may often save ourselves the trouble of weighing the bulb before and after the experiment by determining the weight of the vapour in some other fashion. For instance, if the vapour density of iodine is required, we have only to wash out the bulb with a solution of potassium iodide after the experiment has been made, and to titrate the resulting solution with sodium thiosulphate in order to get a very exact determination. Such expedients, however, have been as yet almost entirely neglected.

At very high temperatures, where glass is not sufficiently resistant, porcelain bulbs are used which may be closed by means of the oxyhydrogen blowpipe. As the determination of the temperature in such circumstances is by no means easy, we may avoid it by making a parallel experiment under the same conditions with air, the weight of which is also determined, preferably by measurement rather than by direct weighing. However, if weighing be preferred, a heavy gas of known density ought to be employed instead of air, in order to reduce the relative error of weighing. Iodine vapour, hitherto used for this purpose, is not suitable, as its density at high temperatures is not constant. (Deville and Troost.)

In a certain sense the converse of Dumas's process constitutes the method of Gay-Lussac, in which we determine, not the quantity of vapour which occupies a given volume, but the volume which is occupied by a given quantity of vapour. The method presupposes the possibility of weighing the substance in the solid or liquid state.

In the actual performance of the experiment, such a weighed quantity is introduced into a graduated glass tube filled with mercury and standing in a mercury trough. The tube must be placed in an apparatus which allows of its being maintained at a uniform temperature which can be accurately determined. The substance assumes the vaporous state, whereby mercury is displaced, the displaced volume being read off on the divided scale. The pressure on the gas is equal to that indicated by the barometer minus the height of the column of mercury still remaining in the tube; this height must, however, be reduced to  $0^\circ$  by making use of the known coefficient of expansion of mercury (0.000182).

A variation of this method given by Hofmann, who employs long tubes and a vapour-jacket for heating, is a great improvement on the somewhat inconvenient original process.

To this group also belongs Victor Meyer's method, which is likewise a very convenient one. A cylindrical vessel with a long neck is heated to a suitable uniform temperature. The upper part of the vessel is put into communication with a measuring tube, and then a weighed quantity of the substance is let fall into the lower part of the apparatus. The substance in assuming the gaseous state expels an equal volume of the air which filled the vessel; this air enters the

measuring tube, and from the reading its weight can be determined in the usual way. The method has the great advantage of being applicable at all temperatures for which resistant vessels can be made, and of a knowledge of the temperature of the vapour-chamber not being required. This temperature must, however, remain constant during the experiment.

In order to learn the temperature of the vapour-chamber, which is of importance for certain purposes, Victor Meyer drives out the contained air by means of hydrochloric acid gas and collects it over water. If  $v'$  is the volume of the air expelled at the temperature of the atmosphere  $t'$ , and  $v$  the volume of the vapour-chamber, then the required temperature  $t$  follows from Gay-Lussac's Law.

$$v' : v = (1 + \alpha t') : (1 + \alpha t),$$

$$t = \frac{v - v' + .00367 t' v}{.00367 v'},$$

Other methods, to be used in special cases, have been frequently described, but they have not come into general use, and so may be neglected here.

## CHAPTER III

### GAY-LUSSAC'S LAW OF VOLUMES AND AVOGADRO'S HYPOTHESIS

IN the course of experiments on the proportions by volume in which oxygen and hydrogen combine to form water, it was found at the end of last century that the ratio was 1:2. That they combined exactly in this proportion, as nearly as the experimental resources of that age allowed to be determined, was first enounced by Gay-Lussac and Humboldt in 1805. Three years later Gay-Lussac established in a memoir afterwards famous that this was only a special case of a law that held for all gases. The law runs thus: If gaseous substances enter into chemical combination, their volumes are in simple rational proportions, and if a gaseous substance is formed by their union, its volume also is rationally related to the volume of the original gases. All the volumes must, of course, be measured at the same temperature and pressure.

This law evidently allows us to calculate the densities of gaseous compounds from those of their elements, if we know the volume relations on their formation. Two vols. hydrogen and 1 vol. oxygen give 2 vols. aqueous vapour. Now the specific gravity of hydrogen (air = 1) is  $\cdot 0693$ , *i.e.* the same volume that contains one gram of air at a given temperature and pressure\* will contain only  $\cdot 0693$  g. of hydrogen. The specific gravity of oxygen is  $1\cdot 1056$ . We calculate now as follows—

2 vols. hydrogen weigh	$\cdot 1386$ g.
1 vol. oxygen weighs	$1\cdot 1056$ g.

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The resulting 2 vols. aqueous vapour weigh  $1\cdot 2442$  g.  
Consequently 1 vol. „ „ weighs  $\cdot 6221$  g.  
Observation gives  $\cdot 623$  g. an almost identical number.

If we consider that gases combine by weight in the proportion of their atomic masses or multiples of them, and now also in equal or

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\*  $773\cdot 3$  c. cm. under normal conditions (cf. p. 48).

multiple volumes, then we see that the weights of equal volumes of gases, or their specific gravities, must be to each other as their atomic weights or multiples of their atomic weights.

The idea is not far to seek, so to choose the atomic weights that their rational factors will agree with those of the volumes in chemical combinations. Then the weights of equal volumes of the various gases will be to each other as the weights of their atoms. That this may hold, there must be the same number of atoms in equal volumes of different gases. Such an idea receives great support from the general behaviour of gases. That they all behave alike as regards changes of temperature and pressure, independent of their chemical nature, leads us to the conclusion that their mechanical constitution must be similar, which is evidently the case if they all contain the same number of atoms in equal volumes, the atoms being, under the same external conditions, equally distant from each other.

However, one difficulty militates so strongly against this simple assumption that we have no option but to let it drop. When chlorine and hydrogen unite to form hydrochloric acid gas, the volume remains unchanged, *i.e.* one litre of chlorine and one litre of hydrogen give two litres of hydrochloric acid. If the number of chlorine atoms in a litre is  $N$ , then according to the hypothesis the number of hydrogen atoms is likewise  $N$ , and that of the hydrochloric acid atoms formed can be no other than  $N$ , as each chlorine atom gives with each hydrogen atom one atom of hydrochloric acid. The volume of the hydrochloric acid ought therefore to be one litre; but it is two litres. And yet hydrochloric acid gas follows the laws of Boyle and Gay-Lussac—has therefore undoubtedly the same mechanical constitution as the elementary gases.

In this argument, which appears unanswerable, we have nevertheless tacitly made an assumption that can scarcely be granted without further consideration, *viz.* that the atoms, as such, directly condition the mechanical constitution of gases. As we conceive matter in general to consist of ultimate particles, gases are of course included in this conception, and we must assume in addition that the ultimate particles of gases do not cohere to each other; for a gas as a whole is not coherent, but fills any volume which may be offered to it, assumes any form, passes through any opening, and so forth. It is true that the first assumption to make is that the atoms are identical with these independent ultimate particles, but this is not at all necessary. The independent particles of a gas may consist of a definite number of chemical atoms, united to form a coherent group, nay, this assumption is almost exacted by well-known facts.

We may mix oxygen and hydrogen without their combination taking place; this only occurs at a high temperature, but then with great violence. If gases consisted of separate atoms, such a state of things would be incomprehensible, for there is no ground why these atoms, obeying their so-called



forces of affinity, should not unite to form water. But, on the other hand, if gaseous oxygen and hydrogen consist of groups of atoms, within which the atoms are bound to each other, the bonds must first be loosed before a rearrangement can take place, and it is quite conceivable that such a transformation can only be brought about by the relaxative influence of a high temperature.

If we now assume that the atoms in a gas join to form equal groups, which we shall call molecules, the above considerations regarding the mechanical constitution of gases will hold for these and not for the atoms. We have thus to assume that under the same conditions the molecules of different gases are equally distant from each other, so that equal volumes of the gases contain the same number of molecules.

The difficulty raised above in the case of hydrochloric acid now disappears. The simplest assumption (and this will be shown later to be the correct one) is that the molecules of the gases in question are made up of two atoms. If there be in a litre of chlorine or of hydrogen  $N$  such molecules, there are on the whole  $2N$  atoms of chlorine and  $2N$  atoms of hydrogen present, which by their union give  $2N$  molecules of hydrochloric acid gas, supposing one molecule of it to contain one atom of chlorine and one atom of hydrogen, and this number must occupy two litres, which is the result obtained by experiment.

It is thus possible by means of this hypothesis, for which we are indebted to Avogadro (1811), to explain the law of combining-volumes by the atomic theory, just as we previously explained the law of combining-weights by its help. We have been obliged to introduce a new conception, that of the molecule, in order to do this; but the molecular hypothesis has proved extremely fruitful, and has contributed no less to the advancement of science than the atomic hypothesis of Dalton.

Gay-Lussac's law of Volumes will now run: The specific gravities of gaseous substances stand to each other in the ratio of their molecular weights.

The number that expresses the relation between the vapour density and the molecular weight manifestly depends on the unit we use for each. The values of the molecular weights are given by the atomic weights; it is therefore best to choose the unit of specific gravity so that the number will be unity, and the specific gravity become equal to the molecular weight. The standard gas would then require to have its molecular weight = 1, *i.e.* it would have to be thirty-two times lighter than oxygen, whose molecular weight is  $32 (= 2 \times 16)$ . But one c. cm. of oxygen weighs  $\cdot 001430$  g. (p. 47); one c. cm. of the hypothetical standard gas would thus weigh  $\cdot 00004469$  g. and the formula for the vapour density  $M$  (cf. p. 48) becomes

$$M = \frac{W76(1 + \cdot 00367t)}{\cdot 00004469pv},$$

or

$$M = 1700000 \frac{W(1 + .00367t)}{pv}.$$

As one c. cm. of air weighs .001293 g., the molecular weights calculated from the foregoing formula are .001293 : .00004469 = 28.94 times greater than the specific gravities compared to air as unity, so that from these specific gravities we obtain the molecular weights by multiplying by 28.94.

In the following table the vapour densities of the elements hitherto determined are collected—

	Atomic Weight.	Molecular Weight.	Ratio.
1. Oxygen . . .	16	32	2
2. Hydrogen . . .	1	2.005	2.01
3. Nitrogen . . .	14.01	28.11	2.01
4. Chlorine . . .	35.45	70.9	2.00
5. Bromine . . .	79.96	159.9	2.00
6. Iodine . . .	126.86	253.0	1.99
7. Sulphur . . .	32.06	65	2.06
8. Selenium . . .	79.1	160	2.03
9. Tellurium . . .	125	254	2.03
10. Phosphorus . . .	31.0	129	4.02
11. Arsenic . . .	75.0	301	4.05
12. Mercury . . .	200	202	1.01
13. Cadmium . . .	112	114	1.02
14. Zinc . . .	65.4	68	1.04
15. Potassium . . .	39.1	37.7	.96
16. Sodium . . .	23.0	25.5	1.11

As we see from these numbers, the atomic and molecular weights always stand in a simple ratio.\* The majority of the elements investigated give the ratio 2, *i.e.* we assume that their molecules consist in the gaseous state of two atoms. For chemical reasons the atomic weights of phosphorus and arsenic have been fixed at a fourth of their respective molecular weights; their molecules are thus composed of four atoms. The atomic and molecular weights of the last five elements, which are all metals, are identical; their molecules, therefore, contain only single atoms.

These are of course hypothetical assumptions. They allow us, however, to represent all the volumetric relations of the gaseous compounds of these elements in a connected and consistent manner.

This is very apparent when the observed densities of gaseous compounds of the foregoing elements are compared with those calculated on the assumption that the molecules of compound substances are in general represented by the simplest of the possible chemical

\* The deviations from whole numbers in the last column are caused by the gases and vapours investigated not exactly obeying the laws of Boyle and Gay-Lussac.

formulae. The molecular weight is then equal to the sum of the atomic weights of the elements contained in the compound.

As most vapour densities have been determined relatively to air, the corresponding theoretical values in the following table have been obtained by dividing the molecular weight by 28·94—

	Molecular Weight.	Density (air=1).	
		Calculated.	Observed.
Water, $\text{H}_2\text{O}$ . . . . .	18	·623	·623
Ammonia, $\text{NH}_3$ . . . . .	17·04	·589	·590
Nitrogen monoxide, $\text{N}_2\text{O}$ . . . . .	44·08	1·524	1·527
Hydrochloric acid, $\text{HCl}$ . . . . .	36·46	1·264	1·26—1·28
Chlorine peroxide, $\text{ClO}_2$ . . . . .	67·46	2·34	2·37
Nitrosyl chloride, $\text{NOCl}$ . . . . .	65·54	2·27	2·33
Hydriodic acid, $\text{HI}$ . . . . .	129	4·42	4·44
Hydrogen sulphide, $\text{H}_2\text{S}$ . . . . .	34·0	1·18	1·19
Sulphur dioxide, $\text{SO}_2$ . . . . .	64·0	2·22	2·25
Sulphur monochloride, $\text{S}_2\text{Cl}_2$ . . . . .	134·9	4·68	4·70
Hydrogen selenide, $\text{H}_2\text{Se}$ . . . . .	81·1	2·77	2·80
Hydrogen phosphide, $\text{H}_3\text{P}$ . . . . .	34·0	1·18	1·17
Phosphorus trichloride, $\text{PCl}_3$ . . . . .	137·4	4·76	4·88
Phosphorus oxychloride, $\text{POCl}_3$ . . . . .	153·4	5·33	5·33
Phosphorus sulphochloride, $\text{PSCl}_3$ . . . . .	169·4	5·88	5·90
Phosphorus pentasulphide, $\text{P}_2\text{S}_5$ . . . . .	222·3	7·72	7·67
Hydrogen arsenide, $\text{H}_3\text{As}$ . . . . .	78·0	2·70	2·70
Arsenic trioxide, $\text{As}_2\text{O}_3$ . . . . .	396·0	13·72	13·78
Arsenic trichloride, $\text{AsCl}_3$ . . . . .	181·4	6·27	6·30
Mercuric chloride, $\text{HgCl}_2$ . . . . .	271·3	9·39	9·8
Mercuric bromide, $\text{HgBr}_2$ . . . . .	360·3	12·48	12·16
Mercuric iodide, $\text{HgI}_2$ . . . . .	454·1	15·7	15·6
Cadmium bromide, $\text{CdBr}_2$ . . . . .	172·0	9·40	9·3

Here again the two last columns agree within the limits of experimental error, and therefore confirm the assumptions made above.

The law can, however, be still further extended, for without new assumptions we see that the vapour density of all compounds, even although they contain non-volatile elements, must be proportional to the sum of the atomic weights of their components, or equal to a 28·94th part of this (the molecular weight) if we take air = 1. We find this also completely confirmed by experiment.

	Molecular Weight.	Density (air=1).	
		Calculated.	Observed.
Methane, $\text{CH}_4$ . . . . .	16·0	·554	·555
Carbon dioxide, $\text{CO}_2$ . . . . .	44·0	1·524	1·529
Silicon tetrachloride, $\text{SiCl}_4$ . . . . .	169·0	5·87	5·94
Boron trichloride, $\text{BCl}_3$ . . . . .	117·5	4·06	4·02
Aluminium chloride, $\text{AlCl}_3$ . . . . .	133·5	4·60	4·80
Gallium chloride, $\text{GaCl}_3$ . . . . .	176·4	6·08	6·13
Indium chloride, $\text{InCl}_2$ . . . . .	184·7	6·36	6·44

	Molecular Weight.	Density (air = 1).	
		Calculated.	Observed.
Chromyl chloride, $\text{CrOCl}_2$ . . .	155·3	5·38	5·55
Ferrous chloride, $\text{FeCl}_2$ . . .	127	4·38	4·32
Zinc chloride, $\text{ZnCl}_2$ . . .	136·3	4·70	4·61
Cuprous chloride, $\text{Cu}_2\text{Cl}_2$ . . .	197·6	6·84	6·93
Lead chloride, $\text{PbCl}_2$ . . .	277·8	9·64	9·6
Bismuth chloride, $\text{BiCl}_3$ . . .	314·5	10·95	11·4
Thallous chloride, $\text{TlCl}$ . . .	239·6	8·5	8·8
Antimony trichloride, $\text{SbCl}_3$ . . .	226·8	7·90	7·8
Niobium pentachloride, $\text{NbCl}_5$ . . .	271·7	9·4	9·6
Vanadium tetrachloride, $\text{VdCl}_4$ . . .	193·1	6·69	6·69
Tantalum pentachloride, $\text{TaCl}_5$ . . .	359·6	12·4	12·9
Molybdenum pentachloride, $\text{MoCl}_5$ . . .	273·4	9·42	9·46
Tungsten pentachloride, $\text{WCl}_5$ . . .	361·5	12·5	12·7
Uranium tetrachloride, $\text{UCl}_4$ . . .	381	13·2	13·3
Stannous chloride, $\text{SnCl}_2$ . . .	189·0	6·53	6·67
Stannic chloride, $\text{SnCl}_4$ . . .	260·0	8·98	9·20
Titanium tetrachloride, $\text{TiCl}_4$ . . .	190	6·58	6·84
Zirconium tetrachloride, $\text{ZrCl}_4$ . . .	232·6	8·02	8·15
Germanium monosulphide, $\text{GeS}$ . . .	104·3	3·60	3·54
Germanium tetrachloride, $\text{GeCl}_4$ . . .	214·2	7·40	7·44
Germanium tetraiodide, $\text{GeI}_4$ . . .	579·7	20·0	20·5
Potassium iodide, $\text{KI}$ . . .	157·9	5·75	5·85
Thorium tetrachloride, $\text{ThCl}_4$ . . .	374·3	12·93	12·42

The observed and calculated figures show an agreement mostly very satisfactory. It is to be noted that many of these compounds are gasifiable only at a very high temperature, and are some of them very easily decomposed, so that several of the larger variations find their explanation in these circumstances.

The reasons for the choice of the atomic weights given above (p. 32) are now made clear from a consideration of the vapour densities. If we were, for example, to take as the atomic weight of phosphorus  $2 \times 31 = 62$  in order to obtain the formula  $\text{P}_2$  for its vapour, then the composition of hydrogen phosphide would necessarily be  $\text{PH}_6$ , its molecular weight 68, and its density 2·35. But as the last is found to be only half as large, it is thereby shown that the molecular weight of hydrogen phosphide is only 34, and the atomic weight of phosphorus itself not more than 31. The same holds for arsenic and arsenic trichloride.

The case is different with the metals mercury, cadmium, zinc, potassium, and sodium. We can only determine from the vapour density how much the atomic weight of an element can be at most, but in nowise how small it may be. The laws would be equally well obeyed if we were to give mercury the atomic weight 100 and to mercury vapour the formula  $\text{Hg}_2$ . We must here avail ourselves of other laws, which will be discussed in the sequel.

If we glance backwards at the relations which subsist between the volumes and the chemical composition of gaseous compounds, we see

that they are of quite a different type from those which came to light when we considered the mass relations of chemical substances. As has been already mentioned, the latter are purely additive (p. 38), *i.e.* the mass of a compound is the sum of the masses of its elements. With respect to the volume taken up by gases, this property is in a certain sense quite independent of their chemical composition. If we take, for example, a definite volume of hydrogen and transform it into water vapour, its volume is not altered thereby. The water vapour can by combination with ethylene,  $C_2H_4$ , be changed into alcohol vapour,  $C_2H_6O$ ; the volume still remains the same. Ethylene may again be added, so as to give butyl alcohol,  $C_4H_{10}O$ , without a change of volume occurring; and so on. Properties that always retain the same value for definite groups of substances, independent of the chemical nature and number of the atoms in these complexes, I have, at the suggestion of Professor Wundt, named colligative. The volume of gaseous substances, therefore, is such a colligative property.

As we explained the existence of additive properties by the atomic theory, which states that in compounds the component elements remain unchanged each after its nature, so we now explain the existence of colligative properties by the assumption of independent atomic groups, which determine certain relations by their number alone and not by their nature or their chemical composition. The colligative properties thus lead us to the molecular theory, and every such property can be employed to reply to questions regarding the number and size of given molecules, at least relatively.

## CHAPTER IV

### ABNORMAL VAPOUR DENSITIES

WE have till now spoken only of those determinations which confirmed Avogadro's hypothesis that equal volumes of different gases contain the same number of molecules. There have been discovered, nevertheless, a number of substances, though by no means a great number, which appear to form exceptions to the law. However, it has been shown that these exceptions are only apparent, so that instead of contradicting the theory they actually confirm it.

One of the best known examples is to be found in ammonium chloride. According to the formula  $\text{NH}_4\text{Cl}$  it has the molecular weight 53.5, and its vapour density should therefore be 1.85; in reality, however, we only find it somewhat more than half this number, viz. 1.01. The explanation of the inconsistency lies in the fact that the vapour of ammonium chloride does not consist of molecules of  $\text{NH}_4\text{Cl}$  at all, but principally of  $\text{NH}_3$  and  $\text{HCl}$ , into which it has decomposed. The number of molecules, and consequently the volume, is doubled, and the density reduced by half.

The proof that the vapour of sal ammoniac is actually a mixture of ammonia and hydrochloric acid was first given by Pebal in 1862. He showed that on diffusion of this vapour the specifically lighter ammonia diffused much more rapidly than the heavier hydrochloric acid, and that both might be identified by their action on litmus paper. The objections raised against the validity of this experiment have all been subsequently answered. In the same way, *i.e.* by difference in the rate of diffusion, and consequent separation, the presence of decomposition products has been proved for very many other substances that exhibited "abnormal vapour densities," so that every doubt has been removed that such decompositions occasion any too small vapour densities that may exist.

In particular cases the proof has been given in other ways. Phosphorus pentachloride should have the vapour density 7.2 corresponding to its molecular weight 208.3; smaller values, however, are always obtained, which vary greatly with the temperature and pressure

and sink so low as 3.6. That this is caused by decomposition into  $\text{PCl}_3$  and  $\text{Cl}_2$  may be seen from the colour of the vapour. The undecomposed vapour of the pentachloride has a very faint colour, if any, while chlorine is green. It was found that the vapour from the pentachloride was likewise green, and that the green became deeper the smaller the density grew, *i.e.* the more free chlorine was split off.

Just as the irregularities observed in compounds may be explained by incipient decomposition into simpler components with corresponding increase in the number of molecules, so certain exceptional phenomena in the case of the elements are capable of interpretation in the same manner.

The vapour density of sulphur was found by Dumas to be 6.6 at  $500^\circ$ , whereas according to analogy the density 2.2, corresponding to the formula  $\text{S}_2$  and the molecular weight 64, was to be expected. When the experiments were repeated at higher temperatures by Bineau, and particularly by Deville and Troost, it was found that the normal value 2.2 was reached at about  $800^\circ$  and remained constant above that temperature. We must, in order to explain this phenomenon, assume that the atoms of sulphur unite at low temperatures to form complex molecules, probably corresponding to the formula  $\text{S}_6$ , which then decompose at higher temperatures.\*

The changes in the density of iodine vapour observed by Victor Meyer (1880) are still more striking. Up to  $500^\circ$  the density has the value 8.8, corresponding to the molecular weight 254 and the formula  $\text{I}_2$ . If the temperature be raised this value continually decreases, until at high temperatures and under diminished pressure the value 4.6 is reached, which nearly corresponds to the formula  $\text{I}$  (Crafts and Meier, 1881).

If we accepted the view that the smallest free particles of iodine vapour consisted of single atoms  $\text{I}$ , then this decrease of density would be inexplicable. We can easily, however, conceive the phenomenon as conditioned by the continual decomposition of molecules of the formula  $\text{I}_2$  (cf. p. 55) into those having the formula  $\text{I}$ , and thus arrive at an intelligible explanation of the matter.

Similar phenomena have been observed in the case of chlorine and bromine, but the decomposition here is not so extensive.

\* H. Biltz has quite recently (1888) investigated the matter more fully. He is of opinion that the great increase in the density of sulphur vapour at low temperature is not due to the formation of complex molecules, but to the near approach to the point of liquefaction. No other example of such a great alteration due to this cause is, however, known, and from the general tenor of Biltz's numbers it would seem much more natural to infer the actual existence of molecules of  $\text{S}_6$ .

## CHAPTER V

### THE KINETIC THEORY OF GASES

THE exceedingly simple mechanical properties which make themselves evident in the uniform comportment of gases towards changes of temperature and pressure have from the first invited attempts to deduce them as necessities by means of some simple mechanical construction. As far back as 1738, Daniel Bernoulli worked out a conception in agreement with that in vogue at the present day. Yet only recently, and in especial by the work of Clausius and Maxwell, has its scope been widened, and applications of it made to various phenomena.

The fundamental phenomenon is the expansive tendency of gases, in virtue of which they fill uniformly any space offered them. No intelligible results were arrived at so long as the existence of a repulsive force between the gas molecules was assumed from analogy with the attractive force of gravitation acting through space. Only when the notion of force was given up, and the property in question conceived as a pure phenomenon of motion, was the framing of an intelligible hypothesis followed by success.

According to this hypothesis a gas consists of a large number of small particles which do not remain at rest each in its place, but move about amongst each other with great velocity. In consequence, as soon as free space is offered to a gas, the molecules already in motion towards that space fly into it, with the result that it is very rapidly filled with the gas. In virtue of this continual movement there is on the average the same number of molecules per unit volume in every part of the space occupied by the gas, *i.e.* the density is everywhere the same.

As the movements take place in all directions, it must happen that molecules in rapid motion attain the walls of the vessel in which the gas is enclosed, rebound from them, and fly back into the interior. Through these continual impacts the gas exercises a pressure on the walls, which manifestly must increase both with the number of molecules and with the mass and velocity of each.

To find this pressure, let us imagine a cube whose side is equal to 1.



Let the number of molecules the cube contains be  $n$ , and let them be all of the same kind, each having the mass  $m$  and moving with the velocity  $c$ . Finally, let the motions take place similarly in all directions.

We consider first one molecule which is flying in any one direction with the velocity  $c$ . According to the laws of kinematics, we may decompose this velocity into three components  $x$ ,  $y$ , and  $z$  at right angles to each other, which are connected with  $c$  by the equation  $x^2 + y^2 + z^2 = c^2$ .

Let the three components be parallel to the edges of the cube. The action which the molecule exercises in striking a side of the cube in the slanting direction with the velocity  $c$  is equivalent to that which it would exercise if it reached the same place with the component velocity perpendicular to the wall in question. If we consider in the first place the component  $x$ , then this action is equal to  $2mx$ , because on striking it must first give up the quantity of motion  $mx$  and then assume the same quantity in the opposite direction when it rebounds, the elasticity being perfect.

This action of a single impact will take place  $\frac{x}{l}$  times in unit time against the two parallel faces of the cube, *i.e.* as many times as the distance in unit time  $x$  is divisible by the distance between the faces of the cube. The total action of a molecule in the unit of time will therefore be equal to  $\frac{2mx^2}{l}$ .

The same holds for the two other components, so that the action of a molecule in unit time on all the faces of the cube will be  $\frac{2m}{l}(x^2 + y^2 + z^2)$ , or, according to the above equation,  $\frac{2mc^2}{l}$ ; and of all the molecules,  $\frac{2mnc^2}{l}$ . To find from this the pressure  $p$  per unit of surface we must divide it by the total surface exposed to the pressure, which in this case is  $6l^2$ ; it follows that  $p = \frac{2mnc^2}{6l^3}$ , or, as  $l^3$  is the volume of the cube,

$$pv = \frac{1}{3}mnc^2.$$

This is the relation developed on the basis of the hypothesis given above as to the mechanical constitution of gases. As in the right-hand member of the equation we have for a given quantity of gas only constant values, it follows that the product of pressure and volume in such a mechanical system must also be constant, and so we have Boyle's Law.

The extension of this proof for the cube to a vessel of any form can be made without difficulty, since the latter may be supposed built up of small

cubes. The internal walls experience equal pressure on both sides, and thus may be imagined altogether absent without the system being changed.

The quantity  $mn$  in the last equation, since it is the product of the mass of one molecule into the number of molecules, is equal to the whole mass of the gas. Half the product of a moving mass and the square of its velocity,  $m\frac{c^2}{2}$ , is called its kinetic energy. Now we can write our equation in the form

$$pv = \frac{2}{3}mn\frac{c^2}{2},$$

so that the result may be expressed thus: The product of pressure and volume of a gas is equal to two-thirds of the kinetic energy of its molecules.

If, therefore, we have different gases at the same volume and pressure, the total kinetic energy of their molecules must be the same.

This evidently holds for every value of the kinetic energy. If now we alter the temperature of a gas, either its pressure or its volume will increase, in general the product of the two. As of the two factors of the kinetic energy, viz. mass and velocity, the first can undergo no change, it is clear that with a change of temperature there must be a change of velocity, and the latter, or rather its square, will be a measure of the temperature.

Two gases are in equilibrium as regards temperature when they do not influence each other on contact with respect to pressure and volume. If we now ask under what circumstances two mechanical systems such as we suppose gases to be, exert no influence on each other (the masses of the moving particles being different), dynamics teaches us that this happens when the kinetic energy of the moving particles is the same; the actual calculation is too involved to be given here. Equal changes of temperature, therefore, in different gases correspond to equal changes of kinetic energy. As, however, on the other hand, the product  $p_v$  is always proportional to the kinetic energy, it follows that in different gases equal changes of temperature cause proportionate changes of the product  $p_v$ . This is no other than the law of the expansion of gases in its most general form, and so it also may be represented as a consequence of our mechanical assumptions.

Lastly, we may deduce Avogadro's Law that in equal volumes of different gases there is under the same conditions the same number of molecules. If  $p_1$  and  $v_1$  be the pressure and volume of one gas and  $p_2$  and  $v_2$  be those of a second, and further if  $p_1 = p_2$  and  $v_1 = v_2$ , then  $p_1v_1 = p_2v_2$ . Now it has been shown that  $p_v = \frac{2}{3}mn\frac{c^2}{2}$ , so we have,

omitting the factor  $\frac{2}{3}$  on both sides,

$$m_1 n_1 \frac{c_1^2}{2} = m_2 n_2 \frac{c_2^2}{2}.$$

According to the proposition mentioned above, two gases have the same temperature when the kinetic energy of their separate molecules is the same, *i.e.* when

$$m_1 \frac{c_1^2}{2} = m_2 \frac{c_2^2}{2}.$$

Dividing the first equation by this one we get

$$n_1 = n_2,$$

*i.e.* if the pressure, volume, and temperature of two gases be equal, then the number of molecules in each is the same. We thus arrive in a perfectly independent although hypothetical way at the same conclusion as we settled upon earlier as being the most probable expression for the chemical facts.

The relations just developed may, lastly, be used to calculate the velocities with which the molecules of different gases must move in order to exercise the pressure actually observed. The equation  $p = \frac{1}{3} mnc^2$  gives

when solved for  $c$  the expression  $c = \sqrt{\frac{3pv}{mn}}$ .

If we consider 1 g. oxygen at  $0^\circ$  and 76 cm. pressure, the mass  $mn$  is in the first place = 1, and the volume of 1 g. oxygen under these conditions is  $v = 699.4$  (p. 47). The pressure is equal to the weight of 1033 g. per sq. cm.; as, however, the intensity of gravitation is 980.5 (any mass receiving through gravity the acceleration of 980.5 cm. per second per second) this magnitude is further to be multiplied by 980.5. If we perform the calculation we find

$$c = 46103.$$

A molecule of oxygen moves, therefore, through space under the given conditions with a velocity of 46103 cm., or over a quarter of a mile per second.

In the formula  $c = \sqrt{\frac{3pv}{mn}}$ , the quotient  $\frac{mn}{v}$ , or the mass divided by the volume, is simply the specific gravity of the gas with respect to water as unity. If this be represented by  $s$ , we have  $c = \sqrt{\frac{3p}{s}}$ ; the molecular velocities of gases are inversely proportional to the square root of their densities.

We have no means of observing these velocities directly, but if different gases be allowed to stream through a small opening in a thin wall, the velocities with which they do so are inversely proportional to the square root of their densities. This is indeed no direct support to our hypothesis, for a

general dynamical consideration shows that this must be the case, without any assumption as to the constitution of gases being made at all. It is, however, noteworthy that the kinetic theory of gases, in so far as the velocity of effusion is considered as conditioned by the velocity of the molecules, leads to the same conclusion.

It might be asked how, in spite of these enormous velocities, a strongly smelling gas developed in one end of a moderately large room filled with still air is not immediately perceptible at the remote end, but requires a sensible time to arrive there. In fact this question has been raised as a decisive objection to the admissibility of the kinetic theory.

Clausius answered it by drawing attention to the circumstance that though the molecules actually possess such velocities in their free paths, yet these free paths are in all probability very short on account of the frequent collisions of the molecules with each other. The actual path of a molecule is thus not a long straight line, but an irregular zigzag composed of very short straight lines, on which the molecule, despite its great velocity, is in general not far removed from its starting-point.

A second question is, whether, if this be the case, it is admissible to assume that all the molecules of a gas have the same velocity. By such incessant collisions some molecules must evidently acquire a greater velocity and others a smaller, so that in general at a given instant there will be all possible velocities in one and the same gas.

We must grant this. But the above deductions still hold, if we determine the velocity  $c$  so that the total kinetic energy of the molecules, if they all had this same velocity  $c$ , would be equal to the kinetic energy they actually possess. Instead of the expression "kinetic energy" we should, strictly speaking, substitute "average kinetic energy" in the above deductions. This of course does not in any way alter the general results arrived at.

Clerk Maxwell calculated the distribution of the velocities for a mechanical system such as we have assumed, if a fixed state were established. The expression can only be deduced in a very complicated manner, and has the form

$$y = \frac{4}{\sqrt{\pi}} \cdot x^2 \cdot e^{-x^2},$$

where  $y$  represents the probability that a molecule has the velocity  $x$ , if the most probable velocity is put equal to unity;  $\pi$  is the ratio of the circumference of a circle to its diameter, and  $e$  the base of the natural logarithms.

This result, that the different molecules of a gas must have different velocities, abstract as it appears on account of our inability to measure these velocities, is nevertheless of great value for the right comprehension of many chemical processes. It teaches us that the molecules of a homogeneous gas (and the same thing applies to liquids) are in no-wise all simultaneously in the same state, but rather in very different states. When, therefore, a substance must be in a certain definite state in order to exhibit some particular chemical action, only a small part of the molecules will in general be in the requisite condition, and a certain time will elapse before all the molecules will have reached this

state. But this is just what our everyday chemical experience teaches; reactions all require a greater or less time for their completion, although it is so small in the case of the apparently instantaneous reactions that it is sometimes of extreme difficulty to prove its existence.

From these considerations we can picture to ourselves somewhat more exactly the nature of a gas according to the kinetic hypothesis. The molecules are moving in all directions with very different velocities and are continually encountering each other. We must for given conditions assume a mean free path which the molecule pursues undisturbed before it comes in contact with another. The molecules will evidently encounter one another all the more seldom the farther apart they are, and all the more frequently the larger their cross section. The mean free path  $L$  is thus directly proportional to the space allotted to each molecule, *i.e.* to  $\frac{1}{n}$ , if we designate by  $n$  the number of molecules in unit volume. It is further inversely proportional to the cross section  $\zeta^2$  of the molecules, if we understand by  $\zeta$  the distance closer than which the centres of gravity of two molecules cannot approach. The exact expression is given by O. E. Meyer in the form

$$L = \frac{1}{\pi \sqrt{2} \cdot n \zeta^2}.$$

$\zeta$  and  $n$  are both unknown, but from the phenomenon which led us to the question of the free path, *viz.* from the velocity with which one gas penetrates into another, the velocity of diffusion, we may draw conclusions as to their magnitude. The theory of these processes, as well as of the nearly related phenomena of gaseous friction and conduction of heat, is still by no means completely worked out, in spite of many efforts in this direction; yet we have got so far that the values of the free paths determined in different ways agree pretty well with each other. They are extremely small, in the case of air, for example,  $\cdot 00001$  cm., a length falling without the limits of the microscopically visible.

When  $L$  has been determined, then, as may be seen from the equation, we are in a position to calculate  $n\zeta^2$ , the sum of the cross sections of all the molecules contained in unit volume. In this way we find that these cross sections amount to more than  $1\cdot 5$  sq. metres in 1 c. cm. of air. This comes from the enormous number and small size of the molecules, for the more finely a mass of given density is divided the larger will be the total cross section of its particles.

Lastly, the dimensions of the molecules themselves have also been calculated. The method of doing so will be given later; here it will suffice to note the result, which is that the diameter of a molecule lies in general between the limits  $10^{-7}$  and  $10^{-8}$  cm.

If the molecules in a given mass of gas take up a measurable part of the space, this circumstance must have an influence on the validity of Boyle's Law. For example, if the diameter of a molecule moving at right angles to two parallel walls of a cube be a hundredth part of the distance between them, the number of encounters will evidently be greater than if the molecule possessed no extension, for the molecule has each time to traverse, not the whole distance between the walls, but that distance minus its own diameter. The pressure will therefore, on account of this circumstance, increase more rapidly with decreasing volume than Boyle's Law requires.

A correction for this may be easily introduced. If  $b$  be the space occupied by the molecules, then Boyle's Law does not apply to the whole volume  $v$  of the gas, but to the space not occupied by the substance of the molecules,  $v - b$ , and instead of the equation  $p v = R T$  we get

$$p(v - b) = R T.$$

This correction  $b$  is of all the greater importance the smaller the volume is in which the gas is confined, and therefore can only be accurately observed at high pressures. It explains the irregularities which Regnault observed in the case of hydrogen, and which, according to the researches of Natterer and Amagat, appear in all strongly compressed gases (p. 42). In this way Budde (1874) calculated that for hydrogen, for instance, the molecules occupy 00082 of the total volume at a pressure of 100 cm. of mercury.

Now the total cross section of the hydrogen molecules in a cubic centimetre at 76 cm. pressure, according to the calculations given above, amounts to 9500 sq. cm. If we call  $x$  the side of a molecule supposed cubical in form,  $9500x$  must be equal to the total volume of the molecules, *i.e.*  $00082 \times \frac{76}{100} = 00062$  c. cm., whence  $x = 6 \times 10^{-8}$  cm., a value within the limits given above.

Besides this deviation from Boyle's Law at high pressures, all gases except hydrogen exhibit another one in the opposite sense which is especially evident at medium pressures, the observed volume being too small. To explain this, it is assumed that the mutual attraction of the molecules which causes their coherence in the solid and liquid states comes also into play in the case of gases, and neutralises a portion of the pressure which is caused by the motion of the molecules. Van der Waals (1879) developed a theory, according to which this interaction is inversely proportional to the square of

the volume; to the external pressure we must therefore add a quantity  $\frac{a}{v^2}$ , so that the gas equation now assumes the form

$$\left(p + \frac{a}{v^2}\right) (v - b) = R T.$$

This corrected equation finds its chief application in the passage from the gaseous to the liquid state, and will be more particularly studied in the sequel.

## CHAPTER VI

### THE SPECIFIC HEAT OF GASES AND THE FIRST LAW OF THERMODYNAMICS

WHEN a given quantity of gas is heated, it requires a definite amount of heat to impart to it a definite rise of temperature. The ratio of the last two values, taken for unit mass of the gas, is called its specific heat. If the change of temperature is represented by  $dt$ , the heat communicated by  $dQ$ , then the specific heat  $c = \frac{1}{m} \cdot \frac{dQ}{dt}$ , where  $m$  is the mass of the gas.

Quantity of heat is measured in terms of the calorie as unit, *i.e.* of that quantity which is required to raise the temperature of 1 g. of water  $1^{\circ}$  C.

The specific heat of air, for example, is found to be equal to .2375 when the experiment is so conducted that air is warmed in a system of tubes to a definite temperature higher than that of the liquid in a calorimeter, to which it is then made to give up the excess of heat, being all the time under the same pressure.

But the following experiment is well known. If an enclosed quantity of air is suddenly compressed, its temperature rises. No heat is communicated, and the change of temperature is finite, therefore the quotient  $\frac{dQ}{dt}$ , and consequently the specific heat, vanishes. If

we allow a quantity of air to expand, it becomes colder. If we communicate so much heat to it that its temperature remains constant, then  $dQ$  has a finite value, while  $dt$  is zero; the specific heat is therefore infinite. If we thus let the gas change its volume, the conception of specific heat becomes indefinite; the specific heat can assume any value whatever.

On the other hand, Gay-Lussac (1807) made this experiment. Air was compressed in a hollow sphere, while another similar sphere was exhausted by the air-pump. When the two spheres were placed in the water of a calorimeter, and then connected with each other so

that the compressed air could expand into the vacuum, no change in the temperature of the calorimeter took place. The change of volume alone, therefore, does not cause the change of temperature.

J. R. Mayer in 1842 reconciled these two apparently contradictory facts. To the questions: Whence comes the heat generated on the compression of a gas, and what becomes of the heat which vanishes when a gas expands? he gave the answer: The work that is done during the compression is changed into heat, and the work that the gas does in moving back the external air pressing upon it cannot spring into existence from nothing, but comes from the heat which the gas loses. If there is no external pressure to overcome, as in Gay-Lussac's experiment, there is no work to be done and consequently no heat is used up.

Work and heat appear here as two forms of the same thing, like red and yellow phosphorus, or like diamond and amorphous carbon. The thing itself Mayer conceived as uncreatable and indestructible, constant under all conditions; it could only suffer change in apparent quality, none in quantity. He called it "force." But as this name possesses another signification in dynamics than that which Mayer had in his mind, some confusion was caused by his choice. The name energy has therefore been generally adopted to denote this thing and the principle enounced by Mayer is that of the Conservation of Energy.

This principle is derived from experience, and is of the most general significance, like that of the conservation of matter, and just as the vain endeavours of the alchemists to make gold were caused by ignorance of the latter, a like ignorance of the former led to the many attempts to solve the equally impossible problem of the perpetual motion. The fact that it was ever considered possible to create work from nothing, shows that the principle of the conservation of energy is by no means a necessity of thought, as is sometimes alleged. It is, however, along with the principle of the conservation of matter, the greatest and most comprehensive generalisation ever made in natural science to embrace the observed facts.

We shall later on have occasion to refer repeatedly to the proofs of the principle, which are exceedingly numerous and have never shown an exception. Here we need only mention the experiments of Joule (1843), which form a good example of the connection between the two forms of energy, heat and work, and have led to the determination of the numerical relation between them.

In dynamics we understand by work the product of a force into the space through which the point under consideration has passed in the direction of the force. If we take for practical unit of force the force with which a gram of any substance is attracted by the earth,\* then

\* The so-called absolute unit of force is that which communicates unit speed (a centimetre per second) to unit mass (a gram) during unit time (a second). The unit just employed is 980.5 times greater, as 1 g. receives from gravitation in 1 second a speed of 980.5 cm. per second.



the work which  $m$  grams weight perform when they cover a distance of  $l$  centimetres downwards is  $ml$  units. Now Joule used the work of such weights to rub two iron plates, immersed in water, against each other. As these experience no permanent change, the work expended is transformed into heat, the quantity of which may be calculated from the mass and rise of temperature of the water. If we now put this quantity of heat equal to the work expended, we obtain, as Joule found, a perfectly constant ratio between them, which depends neither on the mode of changing the work into heat nor on any other condition of the experiments. The mean value of the ratio from frequently repeated determinations is

$$1 \text{ calorie} = 42350 \text{ g. cm.},$$

*i.e.* when the product of weight and height amounts to 42350, then 1 g. of water is warmed  $1^\circ \text{C.}$  by this amount of work. The number is called the mechanical equivalent of heat.

Mayer determined the same magnitude in the following way:—The specific heat of air, when at liberty to expand on being heated, is  $\cdot 2375$ , *i.e.* 1 g. of air is warmed  $1^\circ \text{C.}$  by  $\cdot 2375$  cal. From experiments, which will be described below, it has been found that the specific heat of air when its volume remains unchanged is much less, *viz.*  $\cdot 1683$ . As the air itself is heated to the same extent in both cases, and as according to Gay-Lussac's experiment its temperature does not alter when it expands without doing work, the difference of  $\cdot 0692$  cal. per degree can be nothing else than the energy the air requires in order to perform the work of expanding under atmospheric pressure. This may be calculated as follows—

Let us imagine 1 g. of air contained in a cylindrical tube of 1 sq. cm. section; it occupies 773.3 c. cm. at  $0^\circ$  (p. 48) and expands by  $1/273$  of its volume on rising  $1^\circ$  in temperature, *i.e.* by 2.830 c. cm. An air-tight piston moving in the tube would thus be raised 2.830 cm. The pressure of the atmosphere on 1 sq. cm. is 1033 g. weight (p. 41); the work done is thus  $2.830 \times 1033$ , and is equivalent to  $\cdot 0692$  cal. If the product be now divided by this number, we obtain 42380 for the mechanical equivalent, a value which agrees better with that given above than the accuracy of the data used might lead us to expect.

It is of importance for many purposes to know what work a gas can do when it expands at a constant temperature. In general this work will be expressed by the product of the pressure and the change of volume,  $p\Delta v$  (where  $\Delta v$  is the change of volume); the calculation presents some difficulties when the pressure is not constant. It is convenient for this purpose to represent the relation between the pressure and volume of gases graphically, by tabulating the pressures on a perpendicular straight line and the volumes on a horizontal one. The curve obtained has the property that the product of the co-ordinates of any point is constant—corresponding to the gas equation  $p v = RT$ . Analytical geometry teaches us that the form of this curve is that of the rectangular hyperbola.

The work that is done when the volume changes by  $\Delta v$ , *i.e.* the product  $p\Delta v$ , appears in the figure as a narrow quadrilateral surface  $aa'\beta'\beta$ . The total work performed on expansion between two states of the gas  $\beta$  and  $\gamma$  is therefore the sum of all the narrow quadrilaterals  $p\Delta v$ , and thus equal to the quadrilateral  $a\beta\gamma\delta$ . The calculation results, therefore, in the so-called quadrature of the hyperbola.

This problem cannot be solved by elementary mathematics; we must therefore be content with the general result. If a gas expands at the temperature  $T$  from the volume  $v_1$  to the volume  $v_2$ , always exercising meanwhile the pressure given by the equation  $pv = RT$ , then the corresponding work has the value

$$L = RT \lg \frac{v_1}{v_2}.$$

Here  $\lg$  stands for the natural logarithm, *i.e.* a logarithm to the base  $e = 2.71828$ . The natural may be obtained from the ordinary or decimal logarithms by multiplying the latter by 2.30259.

Returning now to the question of the specific heats of gases, we see that we can only speak of such when we accurately determine what external work is done, if any. The simplest case would evidently be that where external work was altogether avoided, for example where the gas was enclosed in an unyielding vessel and the specific heat determined under these circumstances. Unfortunately this theoretically most simple case has hitherto been experimentally quite impracticable, for the vessel in which the gas must be enclosed, and which necessarily takes part in the heating and cooling, has to be made so massive in order to resist the pressure called forth by the change of temperature, that it is responsible for by far the greater part of the heat exchange, so that the part left for the gas cannot be determined with sufficient accuracy.

Such determinations are therefore conducted so that the changes of temperature take place under constant external pressure. In this way we obtain the specific heat at constant pressure, which we shall call  $C_p$ . Extensive experiments for the determination of this number have been made by Regnault, whose results will be given later. E. Wiedemann repeated some of them, and investigated the changes which the specific heat of many gases, especially those containing carbon, undergoes with change of temperature.

To ascertain from these numbers the specific heat at constant

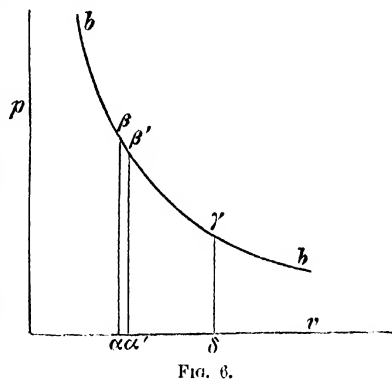


FIG. 6.

volume  $C_v$ , the thermal equivalent of the external work has to be subtracted. The calculation is simplest when such quantities of gas are considered as correspond to the molecular weight in grams, *e.g.* 32 g. oxygen, 2 g. hydrogen. All gases have then the same volume, viz.  $32 \times 699.4^* = 22380$  c. cm. at  $0^\circ$  and 76 cm., and expand on heating by  $1/273$  of this volume or 81.98 c. cm. per degree. The external work amounts to  $81.98 \times 1033$  (p. 70), or 84678 g. cm., and in thermal measure 42350 times less. By chance this last number happens to be almost exactly the half of that just found to represent the work; the external work done by different gases on expanding from  $0^\circ$  to  $1^\circ$  will thus be 2 cal., if we always take such quantities of the gases as are represented by their molecular weight in grams.

The specific heat of gases at constant pressure is usually given for unit weight. To find the external work for this quantity we have only to divide 2 cal. by the molecular weight of the gas. By subtracting the value obtained from the specific heat at constant pressure we get that at constant volume.

It is more suitable, however, for us to calculate the specific heat for molecular weights of the various gases, *i.e.* the molecular heats. They are obtained by multiplying the specific heat for unit weight by the molecular weight. The molecular heats at constant volume are two units smaller than the numbers thus obtained. The values determined by Regnault are given in the following table—

Name.	Formula.	Molecular Weight.	Molecular Heat.	
			At constant pressure.	At constant volume.
Oxygen . . . .	$O_2$	32	6.96	4.96
Nitrogen . . . .	$N_2$	28	6.82	4.82
Hydrogen . . . .	$H_2$	2	6.82	4.82
Chlorine . . . .	$Cl_2$	71	8.59	6.59
Bromine . . . .	$Br_2$	160	8.87	6.87
Nitric oxide . . . .	$NO$	30	6.95	4.95
Carbon monoxide . . . .	$CO$	28	6.86	4.86
Hydrogen chloride . . . .	$HCl$	36.5	6.76	4.76
Carbon dioxide . . . .	$CO_2$	44	9.56	7.56
Nitrous oxide . . . .	$N_2O$	44	9.97	7.97
Water . . . .	$H_2O$	18	8.66	6.66
Sulphur dioxide . . . .	$SO_2$	64	9.82	7.82
Hydrogen sulphide . . . .	$H_2S$	34	8.20	6.20
Carbon disulphide . . . .	$CS_2$	76	11.88	9.88
Methane . . . .	$CH_4$	16	9.42	7.42
Chloroform . . . .	$CHCl_3$	119.5	18.55	16.55
Ethylene . . . .	$C_2H_4$	28	11.95	9.95
Ammonia . . . .	$NH_3$	17	8.60	6.60
Benzene . . . .	$C_6H_6$	78	29.05	27.05
Oil of turpentine . . . .	$C_{10}H_{16}$	136	68.3	66.3
Methyl alcohol . . . .	$CH_4O$	32	14.55	12.55

\* 699.4 is the volume of 1 g. oxygen under normal conditions.

Name.	Formula.	Molecular Weight.	Molecular Heat.	
			At constant pressure.	At constant volume.
Ethyl alcohol . . .	$C_2H_6O$	44	20·7	18·7
Ether . . . . .	$C_4H_{10}O$	74	35·2	33·2
Ethyl sulphide . . .	$C_4H_{10}S$	90	35·8	33·8
Ethyl chloride . . .	$C_2H_5Cl$	64·5	17·55	15·55
Ethyl bromide . . .	$C_2H_5Br$	109	20·20	18·20
Ethylene chloride . .	$C_2H_4Cl_2$	99	22·50	20·50
Acetone . . . . .	$C_3H_6O$	58	23·75	21·75
Ethyl acetate . . .	$C_4H_8O_2$	88	35·0	33·0
Silicon tetrachloride .	$SiCl_4$	169	22·30	20·30
Phosphorus trichloride .	$PCl_3$	137·5	18·35	16·35
Arsenic trichloride . .	$AsCl_3$	181·5	20·20	18·20
Titanium tetrachloride .	$TiCl_4$	190	24·61	22·61
Tin tetrachloride . . .	$SnCl_4$	260	24·15	22·15

Certain regularities may be observed in the preceding table. The molecular heats of the diatomic gases  $O_2$ ,  $H_2$ ,  $N_2$ ,  $NO$ ,  $CO$ ,  $HCl$  for instance are all approximately equal.  $Cl_2$  and  $Br_2$ , however, although likewise diatomic, have considerably higher values. In the same way the gases with three atoms in the molecule partially agree, although with some exceptions. Complete regularity can scarcely be expected, as most of the vapours investigated alter their specific heat considerably and in different ways with the temperature, so that quite dissimilar tables are got according to the temperature of experiment.

The molecular heats at constant volume are, as has been mentioned, calculated by subtracting the external work. They can, however, be experimentally determined in an indirect way, which permits us to measure the ratio of the two specific heats.

The investigations of which we have here to speak took their rise in an enigmatical want of agreement between experiment and what appeared to be a faultless result of calculation. The theory of oscillatory motion in an elastic medium leads, as Newton showed, to the formula  $u = \sqrt{\frac{p}{d}}$  for the velocity of sound in a gas, where  $u$  is the velocity,  $p$  the pressure, and  $d$  the density. For air under normal conditions  $p = 1033$  in gravitation units, or  $1033 \times 980\cdot5$  in absolute units, and  $d = \cdot001293$ . Performing the calculation we get in round numbers 28000 cm. instead of 33100 as obtained by experiment.

Such a want of agreement between the results of mechanical analysis and experience always proves an error to exist in the premisses, and this error Laplace discovered. Newton, in order to introduce the relation between pressure and density, had used Boyle's Law, which makes them proportional to each other. Laplace showed that this was not justifiable, for in the rapid compressions and dilatations which the air experiences during the propagation of sound, the heating and cooling effects mentioned on p. 68 come into play. The pressure thus

increases and decreases faster than the density. The ratio between pressure and density must thus be multiplied by a number which takes account of this influence.

The number may be determined in the following way:—We imagine 1 g. of air under normal conditions contained in a vessel from which projects a cylinder of 1 sq. cm. section; in the cylinder is a piston movable without friction. We press the piston  $\Delta$  cm. into the cylinder, and consequently do the work  $p\Delta$ , producing a quantity of heat equal to  $\frac{p\Delta}{E}$ , where  $E$  is the mechanical equivalent of heat. This heat raises the temperature by  $\frac{p\Delta}{EC_v}$ ,  $C_v$  being the specific heat at constant volume. The pressure would have risen from  $p$  to  $p \left(1 + \frac{\Delta}{v}\right)$  if no heating had taken place; but now it rises besides, owing to the increased temperature, from  $p$  to  $p(1 + at)$ , or, since  $t = \frac{p\Delta}{EC_v}$ , to  $p \left(1 + \frac{ap\Delta}{EC_v}\right)$ ; the ratio of the two increments is

$$\frac{p\Delta a}{EC_v} : \frac{\Delta}{v} = \frac{pva}{EC_v}.$$

If a second compression be now made, the temperature, and with it the pressure, does not rise in the same measure as before, but more rapidly, since the work increases with the now higher pressure. The same holds for all following compressions; if the volume, therefore, is diminished by equal amounts, the pressure will not increase thus equally, but so that the increments increase proportionally with the pressure already existing. This relation is expressed by the formula

$$\left(\frac{v_1}{v_2}\right)^k = \frac{p_2}{p_1}.$$

The exponent  $k$  is the ratio which the total increase of pressure bears to that from Boyle's Law, viz.  $1 + \frac{pva}{EC_v}$ . We can write this in the form

$$k = \frac{C_v + \frac{pva}{E}}{C_v}.$$

Now  $\frac{pva}{E}$  is the thermal equivalent of the external work done by the gas on expanding, for  $1^\circ$  rise of temperature; and the sum of the specific heat at constant volume plus this, is the specific heat at constant pressure, therefore

$$k = \frac{C_p}{C_v}.$$

Processes such as the above, where heat neither enters nor leaves the system, are called adiabatic; here the pressure is not inversely proportional to the volume, but to the  $k$ th power of the volume. By making determinations of the changes of pressure in adiabatic processes

we can calculate from them  $k = \frac{C_p}{C_v}$ , the ratio of the two specific heats. This is as yet the only means we have of arriving experimentally at the specific heat at constant volume.

The sudden alterations of density in the air due to the propagation of sound, being adiabatic, may serve for this purpose;  $k$  is then the correction in the ratio between pressure and density which was found above (p. 74) to be necessary, so that for the speed of sound we must use the formula  $u = \sqrt{\frac{p}{k \cdot d}}$  instead of  $u = \sqrt{\frac{p}{d}}$ . The square of the ratio of the observed speed of sound to that calculated from the old formula is thus equal to the ratio of the specific heats. From the numbers already given we get for air  $k = 1.40$ . With the help of this value the specific heat of air at constant volume used above was calculated, and we saw that the value of the mechanical equivalent of heat obtained from this datum agreed with that determined by direct experiment.

In order to ascertain the speed of sound in other gases than air, and so make the above method applicable to them also, Kundt (1866) contrived a plan for measuring the wave lengths of definite notes produced in tubes by means of the figures assumed by a light powder with which they were dusted internally. If  $l$  is the wave length and  $n$  the number of vibrations of the note in question, then  $nl$  is the velocity of sound. The number of vibrations does not even need to be specially determined, for if waves be produced in air by the apparatus, their length has merely to be divided into the known velocity of sound in air in order to obtain the number of vibrations.

Another method, first applied by Gay-Lussac and Welter, consists in filling a large glass vessel with slightly compressed air and measuring the excess of pressure. A large stop-cock communicating with the external air is then suddenly opened and immediately thereafter again closed. The liquid in the manometer attached, which had assumed the same level in both limbs on the opening of the stop-cock, commences after a few seconds to rise again and remains at a pressure somewhat smaller than the initial pressure. This arises from the cooling of the air consequent on the work it required to do during the sudden expansion. When, after the stop-cock is shut, it reassumes its former temperature from the environment, the pressure increases correspondingly. The calculation of such experiments is made according to the formula on p. 74, which is now written in the form

$$k = \frac{\log p_1 - \log p_2}{\log v_2 - \log v_1}.$$

Experiments of this kind are either more difficult or less exact than those from the speed of sound, as it is very hard to carry out the process quite adiabatically.

If the values of  $k$  obtained in these ways are used to calculate the molecular heats at constant volume from those at constant pressure, the numbers are usually somewhat smaller than the values calculated

from the external work (p. 72). This comes from the assumption there made not holding for the more complicated gases; even on expansion without external work, heat is expended by such gases, although not to any great extent, in partially overcoming during the expansion a sensible interaction of the molecules.

A few words may be said in conclusion on the relation between the kinetic theory of gases and the experimental determinations of the specific heats. Since the product of pressure and volume is equal to two-thirds of the kinetic energy of the moving molecules (p. 63), and this in its turn is proportional to the temperature, it is easy to compute the increase of energy experienced by a gas when heated  $1^\circ$ . It is  $\frac{2}{3}apv$ , where  $a$  is the coefficient of tension  $\frac{2}{3}\frac{1}{3}$ . For a molecular weight in grams of any gas the product  $apv$  has been already calculated (p. 72) and found equal to 2.00 cal.; the energy required for heating this quantity  $1^\circ$  is therefore 3.00 cal. This is the smallest molecular heat that a gas may have at constant volume, and 5.00 cal. the smallest at constant pressure. It has been found that all the experimental numbers are indeed greater than this value.

If now a gas, *e.g.* oxygen, requires 4.96 cal. to heat it at constant volume, then the excess of 1.96 cal. must be expended in doing some sort of work inside the molecule. With the conception we have formed from chemical grounds as to the constitution of most gases, *e.g.* oxygen, intramolecular work must necessarily be assumed; for these systems of two atoms must in their continual impacts receive in addition to their rectilinear motion a motion of rotation round their common centre of gravity, the energy of which will not appear as pressure. It is, moreover, to be expected that with increase of temperature the distance between the atoms in the molecule will increase in consequence of their faster movements of rotation, and this too will require an expenditure of work.

All these things have no place in a gas whose molecules consist of single atoms. Mercury vapour is supposed on chemical grounds to consist of such simple molecules; it should, therefore, possess a molecular heat at constant volume of 3 cal. and at constant pressure of 5 cal., the ratio being 1.67. Neither of the specific heats has been determined, but their ratio was measured by Kundt and Warburg (1876) according to the method given by the former, and found to be 1.66. This is a very good confirmation of the conclusion drawn at first from chemical considerations.

Theoretical investigations have been often undertaken to determine the energy necessary for the intramolecular work in compound molecules, but they have not met with much success. Not only the number but the nature of the atoms has a great influence on the conditions, as may be seen from the fact that the molecular heats of gases containing the same number of atoms in the molecule have been found to be different. A mathematical expression for this influence has not yet, however, been given.

# BOOK III

## THE PROPERTIES OF LIQUIDS

### CHAPTER I

#### GENERAL PROPERTIES

MATTER in the liquid state has lost the property of completely occupying any space offered to it. Liquids, in contrast to gases, possess a definite volume, which it is true may be increased or diminished by change of temperature or pressure, but only in a small measure. Like gases, liquids possess no proper form, but assume at every time that which corresponds to the sum of the forces acting on them.

With respect to the influence of pressure, liquids show nothing of the uniformity that we found in the case of gases. The compressibility, measured by the change of volume which unit volume experiences when subjected to unit pressure, is very small; it is, *e.g.* for water, only about 48 millionths per atmosphere. For other liquids it is mostly greater, and always to a great degree dependent on the temperature. Anything general as to this magnitude can scarcely be stated, as its determination is still very inexact, on account of our inability to calculate with sufficient accuracy the changes of volume which the containing vessels undergo.

The expansion of liquids by heat is also greatly dependent on their nature, and is not yet susceptible of treatment from a general chemical standpoint. The influence of temperature on the volume is commonly represented by an equation having the form  $V = V_0(1 + at + bt^2 + ct^3 \dots)$ , where  $V$  is the volume at the temperature  $t$ ,  $V_0$  the same at  $0^\circ$ , and  $a, b, c, \dots$  constants. Such formulæ have no theoretical significance, and only serve to calculate the volumes for intermediate temperatures at which no direct observations are made. The same service is rendered by curves, whose abscissæ



represent the temperatures and ordinates the volumes, or better, the changes of volume.

Mendelejeff (1884) has proposed a formula which can represent the expansion of liquids by heat with considerable accuracy, although only one constant is used. It has the form  $V = \frac{V_0}{1 + kt}$  and agrees tolerably well with the observations made. The variations from it, however, are mostly larger than can be explained by errors of experiment, and Mendelejeff therefore considers his formula as a law like the laws for gases, which an ideal liquid would follow exactly, but from which actual liquids diverge more or less, according to circumstances. No investigations as to the connection between the magnitude  $k$ —the “modulus of expansion”—and the composition of liquids have as yet been undertaken.

Water occupies quite a peculiar position with regard to expansion by heat, as Rumford showed in 1802. On heating from 0° it contracts until it occupies a minimum volume at 4°, whence on further heating it expands like all other liquids, expanding the more the higher its temperature already is. Between 0° and 100° it expands some four per cent of its volume at 0°, one-fourth of this expansion taking place between 0° and 50°, and the remaining three-fourths between 50° and 100°.

We may finally raise the question of the form which the hypothesis of the molecular structure of matter must take in order to explain the liquid state. Evidently there can be no longer perfect freedom of motion of the molecules as in the case of gases. They must rather be so influenced by each other that they form by means of their internal forces a connected whole, from which, in general, single molecules cannot escape. The proper volume possessed by liquids is conditioned by this. On the other hand the molecules still retain such freedom of motion that each one is not fixed in its place, but can glide about amongst the others without any considerable work; from this arises the capability of liquids to adjust their form with respect to the forces acting on them,—especially under the influence of gravity to fill the lower part of the containing vessel and to form a plane surface. We may admit the molecules of liquids to have, like those of gases, a certain amount of rotary and rectilinear motion; only these motions must be much more limited than in the case of gases.

As different liquids behave differently towards external pressure and heat, it is to be concluded that their volume is not conditioned, like that of gases, by general circumstances which are independent of their chemical nature, but rather by the nature of the molecules and their reciprocal action, which latter we usually represent to ourselves as mutual attraction. The volume of liquids is not a colligative property, like the volume of gases; we shall see later that it is in the main additive in character.

## CHAPTER II

### RELATIONS BETWEEN THE GASEOUS AND LIQUID STATES

If a quantity of gas be exposed to a continually increasing pressure at constant temperature, two things may happen. Either the volume decreases at first somewhat more rapidly than the pressure increases, then at the same rate, and finally more slowly; the greater the pressure now becomes the smaller grows the relative decrease of volume, to be at last reduced to quantities of the same order as those observed in the case of liquids. Or, secondly, the phenomenon begins in the same way with a somewhat greater compressibility than corresponds to Boyle's Law. The deviation from this law, however, does not decrease with increasing pressure, but the gas at a definite pressure suddenly loses its homogeneity and separates into one portion which has become liquid and a second which remains gaseous. From this point it is impossible to raise the pressure by diminishing the volume, for the consequence of a diminution is merely the liquefaction of a further portion of the gas, the pressure remaining constant. Only when the volume becomes so small that the gaseous portion has been entirely converted into liquid does the pressure increase for a diminution of volume, but then the increase is very rapid.

If we start in the opposite direction from a liquid under great pressure and increase the volume, the pressure diminishes at first very rapidly until it has reached a certain value. At this pressure the liquid begins to separate into two portions, a vapour and a liquid, and the pressure now remains unchanged for further increase of volume until the liquid has all assumed the gaseous state. Then again an increase of the volume conditions a fall of pressure, which shortly afterwards begins to obey Boyle's Law and diminish inversely as the volume.

A liquid can thus in general only exist when it is under a definite pressure, which must be equal to or higher than the pressure at which it changes into vapour.\* This pressure is called the vapour

\* There are, to be sure, special cases in which liquids have a transitory existence even below this limiting pressure; these will be spoken of later.

pressure of the liquid in question. It depends on the chemical nature of the liquid and on the temperature. With increasing temperature the vapour pressure of liquids assumes all values between zero and a definite maximum, which lies mostly between 30 and 100 atm. according to the nature of the liquid. If a liquid is under a higher pressure than this maximum vapour pressure, then even at the highest attainable temperatures no separation into liquid and vapour takes place, but the liquid remains homogeneous and expands continuously more and more. The lowest pressure at which this phenomenon begins is called the critical pressure.

It depends upon the temperature which of the two cases specified at the beginning of this chapter will occur—whether the gas may be continuously compressed, or whether it will liquefy at some definite pressure. If we take a liquefiable gas and raise its temperature, its vapour pressure, or the pressure at which it will begin to liquefy, increases. This pressure cannot, however, increase without limit, for when the value of the critical pressure is reached there is no temperature at which a separation into liquid and vapour can take place. The lowest temperature at which this state is assumed, or the temperature at which the vapour pressure is equal to the critical pressure, is called the critical temperature.

Similar considerations apply also to the volume. If we imagine a quantity of liquid to be enclosed in a volume, definite but larger than the liquid occupies itself, this space will be filled partly by the liquid and partly by its vapour. If the vessel is warmed the liquid will expand and a further portion of it be transformed into vapour, until the temperature reaches a point at which the liquid has been all gradually converted into vapour. If the vessel be now of smaller size and the experiment repeated, a higher temperature will be required for complete vaporisation; on still diminishing the volume we at last reach one which is entirely filled by the liquid at its critical temperature, without any space remaining over for vapour. This volume, occupied by the liquid at the critical temperature and under the critical pressure, is called the critical volume.

The recognition of these important relations by which our comprehension of the nature of the states of aggregation has been materially advanced, is due to Andrews (1869).

As may be shown from the above facts, it is possible, starting from a substance undoubtedly in the gaseous state, to obtain a liquid without any discontinuous change taking place during the transformation, and conversely. If we take a gas and heat it to above the critical temperature, we can compress it as much as we please without liquefaction occurring. If we continue the compression until the critical pressure is exceeded and then cool, this pressure being meanwhile maintained, no separation into liquid and vapour can take place, but we find after the temperature has been sufficiently lowered and the pressure taken off that the substance is a liquid. Conversely,

starting from a liquid, we can heat it under a pressure exceeding the critical pressure to above the critical temperature without any separation taking place; if we then increase the volume the substance expands, again without separation, and we have a gas. The liquid and gaseous states are therefore merely the limiting members of a continuous series of possible states, and are in nowise in fundamental opposition.

These relations are rendered very clear by the diagram given by Andrews for carbonic acid, the substance with which they were discovered. In the accompanying figure the pressures, in atmospheres, are plotted on the upright and the volumes on the horizontal axis; each curve corresponds to a certain temperature, noted alongside. The last curve on the right for carbonic acid, that for  $48.1^\circ$ , presents the behaviour of a gas; the volume diminishes regularly with increase of pressure. The next curves, for  $35.5^\circ$  and  $32.5^\circ$ , show on the contrary between 80 and 85 atm. a more rapid decrease of volume than in other parts, but still a definite volume corresponds to each pressure. At  $31.1^\circ$  we have the limiting case; here the curve turns very rapidly at about 75 atm., and at the point of contrary flexure it runs for a moment horizontal; the critical state has been reached. If the compression is carried out at a still lower temperature, then the curve shows a break at the place where liquefaction begins, and remains horizontal, *i.e.* without the pressure changing, until after complete condensation a sharp turn upwards appears; the curve then runs almost perfectly vertical in consequence of the volume of the liquid formed scarcely changing with increase of pressure. At still lower temperatures ( $13.1^\circ$ ) the condensation begins earlier and ends later, so that the horizontal portion becomes longer.

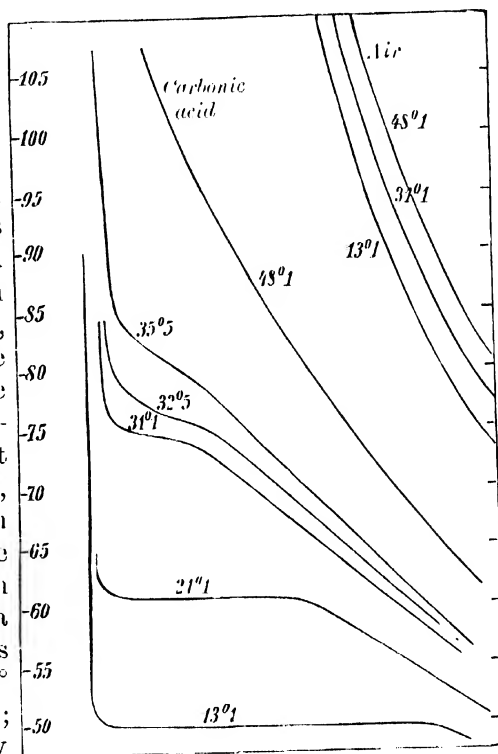


FIG. 7.

It is now possible on the basis of these considerations to distinguish rigorously between gas and vapour; a gaseous body below its critical temperature is a vapour, for it can be liquefied by pressure,

above this temperature it is a true gas, for it can no longer by pressure be reduced to the liquid state. From this we see at once why Natterer, in spite of the enormous pressures he applied, did not succeed in liquefying air and hydrogen; the critical temperature of these substances lying far below ordinary temperatures.

The first to busy himself in a comprehensive way with the task of liquefying the substances known as gases was Faraday (1823). He liquefied carbonic acid, hydrochloric acid, sulphur dioxide, cyanogen, ammonia, and chlorine, by exposing them to considerable pressure at low temperatures. Thilorier (1835) showed how carbonic acid could be liquefied on the large scale, so that it became possible to use the liquid substance, or better the solid mixed with ether, for the production of very low temperatures, down to  $-100^{\circ}$ . Faraday used this means in 1845 and obtained hydriodic acid, hydrobromic acid, sulphur dioxide, hydrogen sulphide, nitrous oxide, cyanogen, and ammonia, not only as liquids but as solids, while hydrochloric acid, hydrogen arsenide, ethylene, silicon fluoride, boron fluoride, and chlorine only assumed the liquid state. Hydrogen, oxygen, nitrogen, nitric oxide, carbon monoxide, and methane, on the other hand, showed no sign of liquefaction.

Afterwards, when the work of Andrews made clear the decisive influence of temperature on the process of liquefaction, the method was of course indicated by which the still resisting gases might be obtained as liquids. Pictet (1877) produced very low temperatures by cooling liquid carbon dioxide by means of sulphur dioxide boiling in vacuo, the former in its turn being then allowed to evaporate rapidly in an exhausted space. Oxygen which was developed in a thick-walled iron retort by heating potassium chlorate, and compressed by its own pressure to several hundred atmospheres, assumed the liquid state at the temperature so obtained ( $-140^{\circ}$ ).

- Caillietet simultaneously liquefied the "permanent" gases by using the work done on their sudden expansion for the purpose of cooling them. To calculate the corresponding changes of temperature we proceed from the adiabatic equation (p. 74),

$$\frac{p_1}{p_2} = \left( \frac{v_2}{v_1} \right)^k$$

As the equations

$$p_1 v_1 = RT_1$$

and

$$p_2 v_2 = RT_2$$

must hold for both the states of the gas given by the indices 1 and 2, we get

$$\frac{p_1 v_1}{p_2 v_2} = \frac{T_1}{T_2}$$

But according to the adiabatic equation  $\frac{v_1}{v_2} = \left( \frac{p_2}{p_1} \right)^{\frac{1}{k}}$ , whence

$$p_1^{\frac{k-1}{k}} = \frac{T_1}{T_2}, \text{ or } \frac{p_1^{k-1}}{p_2^{k-1}} = \frac{T_1^k}{T_2^k}.$$

If we put  $k = 1.41$  for air, then for different initial pressures there is obtained the following table, if we assume the initial temperature to be always  $0^\circ$ , and the final pressure 1 atmosphere.

Pressure in atmospheres.	Temperature.	
	Absolute.	Centigrade.
100 . . . . .	71.5	- 201.5'
200 . . . . .	58.5	- 214.5°
300 . . . . .	52.0	- 221.0'
400 . . . . .	47.9	- 225.1'
500 . . . . .	44.8	- 228.2'

We thus reach very low temperatures by beginning with somewhat high initial pressures. Of course those given in the table are never quite attained, for the gas, which must be in very small quantity on account of the great pressure, is at once warmed by the walls containing it. Liquefaction under these circumstances is simply the production, at the instant the pressure is taken off, of a cloud which vanishes in a few moments.

It was remarked above that in certain cases liquids at definite temperatures can exist under pressures smaller than the vapour pressure at these temperatures. Similarly, vapour may be produced at pressures greater than the vapour pressure corresponding to the temperature. Both phenomena are, however, only possible as long as no vapour is present in the liquid, and no liquid is contained in the vapour. As soon as the least particle of the substance in the other state is present, the separation into liquid and vapour corresponding to ordinary circumstances takes place, and that all the more violently the further the usual limit has been exceeded.

The first case may be most easily observed when drops of water are placed in heated linseed oil. The temperature of the latter may be sometimes raised to  $145^\circ$  before the formation of vapour takes place; with drops of water in mixtures of linseed and clove oil Dufour (1863) reached a temperature of  $175^\circ$ , corresponding to a vapour pressure of 8 to 9 atm.

The second case may be observed by cooling air saturated with aqueous vapour by expansion. In ordinary dusty air a cloud is at once formed, as may easily be seen by wetting the interior of a glass bulb, and then diminishing the pressure of the air inside by suction. If the air has been previously rendered dust-free by filtration or long standing, the formation of a cloud no longer takes place for a small decrease of temperature. These phenomena play an important part in the condensation of atmospheric water vapour and in the origin of thunderstorms.

Both phenomena are examples of a general principle, according to which the separation of heterogeneous parts from a homogeneous mass

does not of necessity follow immediately the conditions are fulfilled under which the heterogeneous parts can exist. There is rather required, besides the presence of these conditions, a special impulse towards the formation of a dissimilar portion, an impulse which may be, however, of very varied nature. Violent mechanical motion is in many cases sufficient to give such an impulse; but the most certain, and in all cases sufficient cause is the presence of a quantity, no matter how small, of the substance which can separate out.

Such phenomena have been mostly considered as being to a certain extent unnatural, and the corresponding states have received the names of superheating and overcooling or supersaturation. They are nevertheless very common, and appear whenever, from a substance or mixture of substances in a homogeneous state, a part may separate out; thus, for example, gases, solids, or immiscible liquids from liquids, or on the other hand liquids or solids from gases. The name "states of instability," which has also been applied in such cases, is equally unsuitable. For the states are not really unstable, since they by no means pass into others on the smallest change. They must rather be compared to the stable equilibrium of a rather tall cylinder standing on one end; the system is certainly stable, but when it suffers a somewhat large displacement it easily assumes another state which is much more stable than the first. It must be admitted, however, that here there is no analogy to the special action exercised by a small quantity of the heterogeneous substance in all the cases above mentioned.

The kinetic molecular theory by which we succeeded in explaining the most essential properties of gases enables us here again to obtain a clear idea of the phenomena just described. It has been already stated (p. 67) that we have reason to assume the presence of mutual attraction between the molecules of gases. This attraction adds itself to the external pressure on the gas and increases, according to van der Waals's assumption, inversely as the square of the volume. The smaller therefore the volume becomes, the larger grows the "internal pressure" of the gas, and on sufficient approximation of the molecules this may reach and even surpass the pressure exercised by the gas towards the exterior by the kinetic energy of its molecules. The consequence is a state in which no external pressure is necessary to retain the volume; the gas has liquefied.

Whether this state will appear or not, evidently depends on the ratio between the internal pressure and the kinetic energy of the molecules. If the latter is very large, *i.e.* if the temperature is high, no possible diminution of volume will produce an internal pressure to balance the pressure due to the energy of the molecular motion; the gas cannot be liquefied. The highest temperature at which this equilibrium of pressure may be instituted is the critical temperature. Only below this can the process of liquefaction take place.

A liquid is thus a molecular system in which the average kinetic energy of a molecule can no longer overcome the internal pressure

caused by the mutual molecular attractions. But all the molecules do not possess this mean kinetic energy (p. 65); there are some with more and some with less. The former coming to the surface of the liquid may break through it and then move about in the free space after the manner of gaseous molecules. This is the process of evaporation. The number of molecules breaking through unit surface depends only on the temperature. If the space over the liquid is unlimited, the gaseous molecules will move away; the liquid must thus get colder, as only the molecules with the greatest kinetic energy, *i.e.* the highest temperature, fly off. If the temperature of the liquid be kept up by external heating, all the molecules will soon assume the gaseous form; the liquid vaporises completely at a rate depending on the relative number of molecules capable of breaking through the surface.

If the space over the liquid is limited, the gaseous molecules rebounding from the walls will soon fly back against the surface of the liquid and be reabsorbed by it. A condition of equilibrium will set in when the number of molecules sent out by the surface is equal to that taken up. The former number depends only on the temperature, the latter on the number and velocity of the gaseous molecules in unit volume. These two last together cause the pressure of the gaseous portion; the equilibrium will therefore take place when the vapour over the liquid exerts a definite pressure which is only a function of the temperature, and increases and decreases simultaneously with this.

The application of the molecular hypothesis is rendered much more complete than these rather qualitative considerations by the use of the corrected gas equation of van der Waals (p. 67). We have

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT.$$

If the equation is multiplied out and arranged according to powers of  $v$ , we get

$$v^3 - v^2 \left(b + \frac{RT}{p}\right) + v \frac{a}{p} - \frac{ab}{p} = 0.$$

It is now of the third degree with respect to  $v$ , and has, according to the values of the constants, either three real roots, or one real and two imaginary. That is, for every value of  $p$  and  $T$  there are either one or three corresponding volumes. The first case evidently holds for the gaseous state where a definite volume exists for every value of pressure and temperature. For temperatures at which the substance can exist both as vapour and as liquid there are manifestly two volumes; a third volume is not known.

If we now construct curves from a series of corresponding values of pressure and volume by tabulating the former as ordinates and the latter as abscissæ, we obtain such as are given in Fig. 8. If these are compared with curves obtained from actual experiment, for instance those drawn by Andrews for carbonic acid (p. 81), we find that below the critical tempera-



ture, instead of the long sinuous curve  $AB\alpha\beta\gamma CD$  which the formula gives, the broken line  $AB\beta CD$  is observed. The straight portion  $B\beta C$  in the

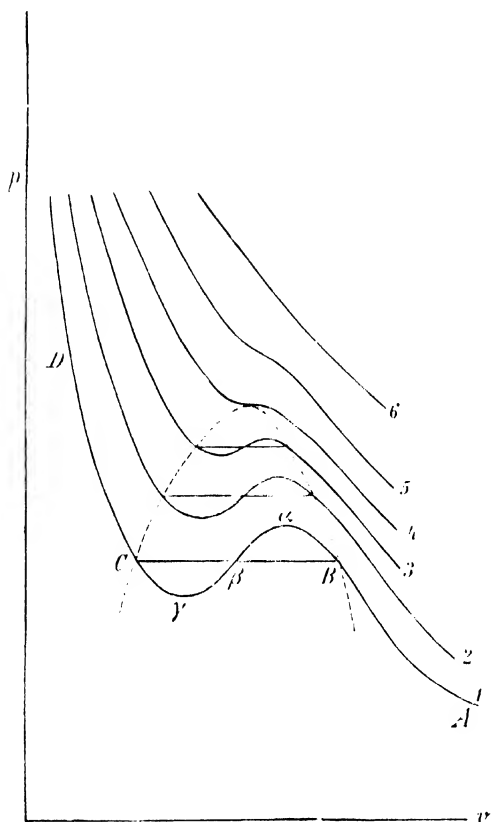


FIG. 8.

middle does not represent the volume of a homogeneous substance, but that of a mixture of vapour and liquid.

The breaks at B and C do not, however, necessarily appear. We have seen (p. 83) that a liquid may exist at a smaller pressure than its own vapour pressure. That means, the curve may be observed prolonged past C towards  $\gamma$ . Similarly, vapour can exist at a higher pressure than the vapour pressure; the curve AB also can thus be prolonged towards  $\alpha$ . This circumstance makes it very probable that the true curve runs continuously, as in the diagram. As far as we can judge, the third volume at  $\gamma$  will never be directly observed. For on the portion  $\gamma\beta\alpha$  the volume would increase with increasing pressure and diminish with decreasing pressure; we would have here to do with veritably unstable states whose realisation seems hopeless.

The formula admits of a particularly satisfactory application to the critical state. In this the volume of the liquid becomes equal to that of the vapour, and each is therefore equal to the inaccessible "third volume." The three roots of the equation (p. 85) have therefore become equal. Now the value  $\phi$  of the three equal roots of an equation of the form  $v^3 - qv^2 + rv - s = 0$  is given by  $\phi = \frac{q}{3}$ ,  $\phi^2 = \frac{r}{3}$ , and  $\phi^3 = s$ .

We have thus  $3\phi = b + \frac{RT}{p}$ ,  $3\phi^2 = \frac{a}{p}$ , and  $\phi^3 = \frac{ab}{p}$ , and if we denote the special values which  $p$  and  $T$  assume in this case by  $\pi$  and  $\theta$ , we have

$$\begin{aligned} \text{the critical volume} & \quad \phi = 3b, \\ \text{the critical pressure} & \quad \pi = \frac{a}{27b^2}, \\ \text{the critical temperature} & \quad \theta = \frac{8}{27} \cdot \frac{a}{Rb}. \end{aligned}$$

These equations are very remarkable. The magnitudes  $a$  and  $b$ , which

were introduced as corrections into the gas equation, can be calculated from the curves on pp. 43-46 so as to represent the variations from the laws of Boyle and Gay-Lussac with sufficient approximation. Once they are got we can determine from them the critical constants, pressure volume and temperature, without making a single direct experiment.

It was natural to test at once the applicability of this result. Van der Waals showed that from Regnault's observations on the compressibility of carbonic acid, the critical temperature  $32\cdot5^{\circ}$  was obtained by calculation, while Andrews had directly determined it to be  $31^{\circ}$ . Such an agreement is indeed a very remarkable confirmation of the theory.

In other cases also the like concordance has been found, and conversely where the critical constants have been directly determined, the variations from the gas equation can be represented with tolerable completeness.

The methods for the experimental determination of the critical constants are as yet but little developed. The critical temperature may be measured most easily by sealing the liquid in a strong glass tube, which it fills to about two-thirds of its capacity, and heating slowly. As the temperature rises we see the meniscus which is the upper boundary of the liquid grow more and more flat and indistinct, until at the critical temperature it vanishes, and a peculiar undulating appearance, mostly in reddish-brown diffraction colours, is seen in the interior of the tube. On cooling slowly there suddenly appears at one place of the seemingly empty tube when the critical temperature is reached, a coloured mist which quickly spreads through the whole space; immediately thereafter it vanishes, and we see the liquid again in the lower part of the tube separated from the vapour-filled space above by a distinct meniscus.

The measurement of the critical pressure and volume is much more difficult. For this purpose the liquid must be placed in a tube of somewhat small bore connected by means of mercury with a manometer which is best filled with nitrogen, as the compressibility of this gas has been very accurately determined by Amagat for high pressures.

A few critical constants are collected in the following table—

	$\theta$	$\pi$	100000 $\rho$	10000 $\alpha$	10000 $\beta$
Ether . . . . .	$190^{\circ}$ C.	36·9	1733	324	57
Carbon disulphide . . . . .	$272^{\circ}$	74·7	1015	219	33
Sulphur dioxide . . . . .	$155^{\circ}$	78·9	744	123	24
Alcohol . . . . .	$234^{\circ}$	62·1	1112	236	37
Ethyl chloride . . . . .	$183^{\circ}$	52·6	1190	227	40
Benzene . . . . .	$281^{\circ}$	49·5	1534	438	51
Acetone . . . . .	$233^{\circ}$	52·2	1329	273	44
Ethyl acetate . . . . .	$240^{\circ}$	42·6	1654	348	55
Chloroform . . . . .	$260^{\circ}$	54·9	1333	287	44
Ethyl formiate . . . . .	$230^{\circ}$	48·7	1429	304	48
Methyl acetate . . . . .	$230^{\circ}$	57·6	1198	248	39
Diethylamine . . . . .	$220^{\circ}$	38·7	1714	355	58
Nitrous oxide . . . . .	$36\cdot4^{\circ}$	37·1	582	74·2	19·4

## CHAPTER III

### BOILING-POINTS

THE boiling-point of a volatile liquid is the temperature at which it can form bubbles of vapour, *i.e.* at which its vapour pressure just begins to exceed the external pressure. This temperature is greatly dependent on the magnitude of the external pressure, changing considerably—by whole degrees—in consequence of the atmospheric variations.

One pressure and the corresponding temperature are not sufficient for the complete determination of a liquid in respect of the pressure of its saturated vapour. All liquids, to be sure, have the property that their vapour pressure increases with rise of temperature; but this increase differs from case to case, and its general law has not yet been found. The attempts to discover it, however, may be shortly noticed.

The first essay was made by Dalton (1801). He gave the rule that liquids having different boiling-points exhibit the same vapour pressure at temperatures removed by the same number of degrees from their boiling-points. Water boils at 100°, ether at 35°, *i.e.* they each have at these temperatures a vapour pressure of 76 cm. At 80°, 20° below the boiling-point, water has the vapour pressure 35.5 cm.; ether, at the corresponding temperature of 15°, the pressure 35.4 cm. The numbers agree admirably; Dalton, in fact, deduced his “law” from the comparison of water and ether. Alcohol, on the other hand, which boils at 78°, has at 58° a pressure of 33 cm., which is considerably too low, and the same holds for most other substances.

Dühring's rule, formed after Dalton's, agrees much better with experiment. It consists in the modification of Dalton's formula by the introduction of a factor depending on the nature of the liquid. When we pass from temperatures of equal pressure to other temperatures of equal pressure, the differences of temperature are not equal, as they would be according to Dalton, but always proportional. In other words, Dalton's rule would hold if a special scale of temperature, proportional to the centigrade scale, were used for each liquid. If we take water as the liquid for comparison, Dühring's formula is

$$t' = \theta + q(t - 100).$$

100 is the boiling-point of water and  $\theta$  that of the liquid at 76 cm.,  $t$  and  $t'$  the boiling-points at any other pressure, and  $q$  a factor which varies, according to the nature of the liquid, between .5 and 2.3. To calculate  $q$

we have  $q = \frac{t' - \theta}{t - 100}$ , i.e. we merely take the ratio of the differences of the boiling-points at any two pressures.

Dühring's formula also is not strictly accurate, although it naturally yields much better approximations than Dalton's. Winkelmann (1880) gives a formula in which the factor  $q$  is not constant but variable, inasmuch as it represents a function of the ratio between the theoretical and the actually observed vapour density at the pressure in question. The formula as far as it has been tested agrees very well with experiment; as it is not without exceptions, however, and is besides as yet without theoretical foundation, we may pass over its detailed development.

General formulæ for vapour pressure have met with still less success than those comparing the vapour pressures of different substances with each other. Countless proposals have been made in this direction, yet no general results have been obtained. The chief reason of this is that the condition of the vapour has been considered determinative of the vapour pressure, whereas the vapour pressure is rather to be looked upon as a function of the nature of the liquid; vapours can exist at greater and smaller pressures; that a certain definite pressure is assumed at a given temperature is caused by the presence of the liquid and numerically determined by its nature.

From the want of general relations in this field, chemistry has had to content itself with setting up numerical relations of a limited character. The first of these was given by Kopp (1842) in the form that equal differences of chemical composition in analogous organic compounds correspond to equal differences of their boiling-points. Every ethyl ether of an acid, for example, boils  $19^\circ$  higher than the corresponding methyl ether, and the acid itself  $45^\circ$  higher.

This observation at once excited great interest and occasioned a considerable number of experiments which were undertaken for the end of establishing general laws, instead of the narrower relations given with due reservation by Kopp. These attempts all came to grief, and necessarily, for their authors considered the boiling-points as directly comparable magnitudes, without inquiring whether, instead of the temperatures of equal vapour pressure, the temperatures of different vapour pressures, depending on the nature of the various substances, were perhaps to be compared. The whole scheme of boiling-points for one pressure changes its form immediately we pass to another pressure.

Later research then has not brought us much further than Kopp's rule given above; indeed the application even of it has had in many cases to suffer restrictions. Metameric substances, for instance, ought by it to have the same boiling-point, but this is not exactly the case. It

has rather been found that the differences in the constitution of isomeric compounds with similar chemical function (differences unknown to Kopp when he published his principle) always determine differences in the boiling-point. Examples of such bodies are to be found in the primary, secondary, and tertiary alcohols and acids; the so-called position-isomers amongst the benzene derivatives, etc. It is true that here also the differences are probably of a regular nature, the primary alcohols boiling higher than the secondary, and these again higher than the tertiary; or, in the other group, the para compounds usually higher than the ortho and meta compounds. These regularities, however, are of a somewhat limited character and admit of so many exceptions that they need here be only indicated.

From the theory of van der Waals (p. 85) a remarkable light is shed on a point already raised, viz. whether boiling-points at the same pressure are comparable. If we put in the general equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

instead of the pressures, volumes, and temperatures measured in the ordinary units, such as are expressed in fractions of their critical values, *i.e.* if we put  $p = \epsilon\pi$ ,  $v = n\phi$ , and  $T = m\theta$  and then substitute for  $\pi$ ,  $\phi$  and  $\theta$  the values given on p. 86, we obtain

$$\left(\epsilon + \frac{3}{n^2}\right)(3n - 1) = 8m.$$

In this equation everything dependent on the particular nature of the substance has vanished, so that it holds (like the gas equation for gases) uniformly for all substances. The equations of condition for all gaseous and liquid substances become the same when the pressure, volume, and temperature are expressed in terms of their critical values.

One restriction, however, must be given at once. Van der Waals's formula is deduced only for the case where the volume of the substance is eight times as large as the magnitude  $b$ ; an assumption for the most part not valid for liquids under the ordinary conditions, their volume being smaller than this. We must not therefore look upon this general relation as necessary, although it may exist in fact. For vapours, on the other hand, it must exist.

Van der Waals has actually shown; *e.g.* in the case of ether and sulphur dioxide, for which the critical constants are known, that at equal fractions of the critical temperatures the vapour pressures amount to equal fractions of the critical pressures.

The formula is not in agreement with that of Dühring, but if we substitute in the latter instead of the boiling-points at the same pressure those at the same fraction of the critical pressures, it passes into that of van der Waals.

## CHAPTER IV

### VOLUME RELATIONS OF LIQUIDS

To express the relation between mass (or weight) and volume we usually employ the specific gravity  $d$ , which is given by the equation  $d = \frac{w}{v}$ , where  $w$  is the weight and  $v$  the volume. The specific gravity is thus the weight of unit volume. But the volume is variable both with temperature and pressure, and the conception of specific gravity is consequently with reference to a variable quantity of the substance considered.

For this reason we cannot use this magnitude and hope to get general results connecting it with the elementary composition of the different substances. We rather employ the reciprocal of specific gravity, viz. specific volume  $\phi = \frac{v}{w}$  which represents the volume of unit weight, and since, in chemistry, not equal quantities but those in the proportion of the molecular weights are comparable, we multiply the specific volume by the molecular weight and thus get the molecular volume  $\mu = m\phi = \frac{mv}{w} = \frac{m}{d}$ . If we express the molecular weight in grams we get the molecular volume in cubic centimetres. As the specific gravity of substances is usually given, we use the last formula for calculating the molecular volume,  $\mu = \frac{m}{d}$ .

The expression "molecular volume" does not signify the "actual" space occupied by the molecule; we are not yet in a position to have definite notions as to this. The molecular volumes are such as contain under the given conditions equal numbers of molecules of the compounds compared.

The first regularities amongst molecular volumes were discovered by Kopp at the same time (1842) as he found the relations between the boiling-points. They admitted of expression in the same form: equal differences in composition correspond to equal

differences in molecular volume. Now the molecular volumes of the organic compounds, which are here chiefly considered, are dependent largely on the temperature, and before any comparison could be instituted it was necessary to decide at what temperature it should be made. Kopp soon found that far greater regularity was obtained by comparing the liquids at their boiling-points rather than at one and the same temperature, say 0°.

Kopp followed up his discovery of the above rule by a long series of exceedingly careful experimental investigations, which served partially to confirm and extend his first observations, partially to restrict them. Generally speaking, the molecular volume at the boiling-point is an additive property; the molecular volume of a compound is the sum of the molecular volumes of its components. At other temperatures, relations of this kind are not so noticeable.

In analogous compounds the molecular volume changes for every  $\text{CH}_2$  by 22 units on the average. This was proved for the hydrocarbons, alcohols, compound ethers, acids, aldehydes, and ketones.

Isomeric liquids have the same molecular volume, as was shown in particular by the comparison of isomeric compound ethers and acids.

When two atoms of hydrogen are replaced by one atom of oxygen the molecular volume is not materially altered. This holds specially for the change of alcohols into acids.

One atom of carbon and two of hydrogen can replace each other without the molecular volume suffering any change. This relation was verified exclusively by the comparison of fatty and aromatic compounds.

These rules at once lead to the idea of ascribing definite atomic volumes to the elements carbon, hydrogen, and oxygen, of which all the compounds mentioned above are composed, so that the molecular volume of the compound may appear as the sum of these atomic volumes. This has proved to be not quite possible, however, the deviations being too large. The property in question is thus not purely additive. Kopp showed how the different modes of combination of oxygen stood in relation to these deviations. When the oxygen is doubly linked to one carbon atom (carbonyl oxygen) the molecular volume is larger than when it is singly linked to the carbon atom (hydroxyl oxygen). If we thus ascribe different atomic volumes to oxygen according to its chemical function, the molecular volumes of the compounds can be represented as the sum of the atomic volumes of their elements, with an error of at most 4 per cent.

The numerical values of the atomic volumes are—

Carbon . . . . .	11
Hydrogen . . . . .	5.5
Carbonyl oxygen . . . . .	12.2
Hydroxyl oxygen . . . . .	7.8

We get, *e.g.* for acetic acid,  $\text{CH}_3\text{CO}(\text{OH})$ ---

$$\begin{array}{rcl} 2\text{C} & = & 22 \\ 4\text{H} & = & 22 \\ \text{O (carbonyl)} & = & 12\cdot2 \\ \text{O (hydroxyl)} & = & 7\cdot8 \\ & & 61\cdot0 \end{array}$$

The observed value is 63·7.

Kopp also fixed the atomic volume of other elements as follows—

Sulphur . . . . .	22·6
Chlorine . . . . .	22·8
Bromine . . . . .	27·8
Iodine . . . . .	37·5
Phosphorus . . . . .	25·4
Silicon . . . . .	32
Arsenic . . . . .	26
Antimony . . . . .	33
Tin . . . . .	40
Titanium . . . . .	35

The last numbers are rather uncertain, as they were derived from only a few compounds.

Very different results were obtained for nitrogen according to the nature of the compounds investigated; no satisfactory explanation has been given of this. The sulphur compounds also exhibited in many cases considerable deviations. These circumstances lead to the conclusion that the influence exercised by the function of the element on its atomic volume is not only to be found in the case of oxygen, but wherever the elements appear combined differently.

Thus Buff (1865) showed that unsaturated compounds have always a somewhat larger molecular volume than that calculated from Kopp's numbers. The same result was afterward obtained by Schiff and Horstmann. The latter also showed the great influence exercised by the chemical constitution in another direction, viz. by the so-called "ring"-formation.

Schiff proved in addition that isomeric compounds have not exactly equal molecular volumes. These usually differ in the sense that the isomer with higher boiling-point has also the greater molecular volume. It was seen simultaneously, from the work of Stadel, that the isomeric chlorine and bromine derivatives of ethane exhibit considerable differences of molecular volume.

All these results point to the molecular volume being influenced in two different ways. On the one hand we have the summation of the atomic volumes of the component elements, so that the molecular volume is from this point of view an additive property. On the other hand the mode of combination of the different elements causes a difference in the amount of space occupied, perhaps in the space taken up by the element itself under these conditions, but more probably in the way the combined elements occupy space together. Properties



like this which depend on differences of chemical combination, or the constitution of bodies, are called constitutive, and the molecular volumes of liquid compounds must therefore be conceived as additive magnitudes subject to constitutive influence.

Besides Kopp's mode of viewing the subject, other modes of representing the actual relations have been proposed by several investigators. As they have not, however, met with any general acceptance, like Kopp's, they need not be detailed here.

I should only wish still to direct attention to two points. First, to the question of comparable temperatures. Horstmann has of late given up the comparison at the respective boiling-points, and recommended instead the comparison at any constant temperature. Kopp has rightly opposed this change on the ground that a number of regularities which undoubtedly appear at the boiling-points must be abandoned. But the boiling-points also, according to the theory of van der Waals (p. 90), ought to be replaced by temperatures which are equal fractions of the critical temperatures.

In reality such a mode of calculation would do away with several existing differences, as may be seen from the few data we possess. To carry this out generally, however, data as to critical temperatures are still mostly wanting.

The general relations of molecular volume have thus been investigated, but nothing has been done to those of expansion by heat. A sufficient measure of comparison for this is probably to be found in Mendeleeff's modulus of expansion (p. 78). It may be predicted that this magnitude will show regularities; for such exist with respect to volume and are undoubtedly not confined to the temperature of ebullition alone.

In conclusion, van der Waals has applied the theory of corresponding states to the expansion of liquids, and arrived at the result that the values for different liquids between equal fractions of their critical temperatures are indeed very nearly equal.

All these researches might be greatly extended by the determination of the critical temperature for a large number of liquids.

## CHAPTER V

### REFRACTION IN LIQUIDS

LIGHT, as is well known, traverses different transparent substances at very different rates. The velocities may be easily ascertained by observing the path pursued by a ray which passes from one medium into another at any angle. The law that the sine of the angle of incidence is in a constant ratio to the sine of the angle of refraction then obtains, and this ratio, called the index of refraction, is that of the velocities of light in the two media.

For the determination of the index of refraction of liquids we employ a hollow prism closed by parallel plates of glass and filled with the substance to be investigated. If we send through such a prism a parallel beam of light which has previously passed through a slit and a lens distant from this by its own focal length, and then search for the diverted image of the slit by means of a telescope focussed for infinity, turning meanwhile the prism so that the deviation is a minimum, then the angle of deviation  $d$  is related to the refractive angle of the prism  $a$  and the index of refraction  $n$  by the following formula,

$$n = \frac{\sin \frac{1}{2}(a + d)}{\sin \frac{1}{2}a}.$$

This is the customary method of determining the refractive index. Another much more convenient process is based on the phenomenon of total reflection—

If  $i$  is the angle of incidence and  $r$  the angle of refraction, then  $\frac{\sin i}{\sin r} = n$ , or  $\sin i = n \sin r$ . If light moves into an optically denser medium from a less dense,  $n > 1$ , and therefore  $i > r$ . For every value of  $i$  there is therefore always a real value of  $r$ . But if light passes from a more into a less dense medium,  $n < 1$ , and therefore  $r > i$ . In this case there cannot be a real value of  $r$  for every real value of  $i$ . If for instance  $n = .8$ , then for angles of incidence having sines  $< .8$  there are possible angles of refraction; for  $\sin i = .8$  we get  $\sin r = 1$ , and therefore  $r = 90^\circ$ , i.e. the ray does not enter the second medium but moves parallel to the plane of separation. For larger

angles of incidence  $\sin i = .8$  and  $\sin r$  would be greater than unity, which is impossible. Here refraction ceases, and reflection takes its place.

The critical angle at which total reflection occurs follows from what has been said; it corresponds to the condition  $\sin r = 1$ , whence  $\sin i = n$ . If this critical angle is determined, the index of refraction is easily found.

The instruments that serve this purpose are commonly called refractometers.

The first apparatus of the kind was described by Wollaston (1801). Convenient instruments have lately been constructed by Abbe and by Pulfrich.

If we observe the deviation of a white ray of light by a prism of liquid, we obtain as usual a spectrum, in consequence of the colours being differently refracted. The index of refraction must therefore be measured for definite rays. The kinds of light mostly employed are given in the following table with their wave lengths in millionths of a millimetre—

Lithium (red)	. . . . .	670.6
Hydrogen (red)	. . . . .	656.2
Sodium (yellow)	. . . . .	585.5 and 588.9
Thallium (green)	. . . . .	534.5
Hydrogen (green)	. . . . .	486.0
Hydrogen (violet)	. . . . .	434.0

The index of refraction of a given liquid is dependent on the temperature as well as on the kind of light, usually decreasing with rise of temperature. It varies also when the specific volume of the liquid is changed by alteration of the external pressure. We must therefore ask if there is no function of the index of refraction which represents the influence of the substance on the speed of light, independent of the volume which that substance occupies.

Several such formulæ have been proposed, but the problem has not been completely solved by any one of them. First of all Newton, from his emissive theory of light, gave the expression  $(n^2 - 1)\phi$ , where  $\phi$  is the specific volume (or the equivalent one  $\frac{n^2 - 1}{d}$ , where  $d$  is the density). This formula lost all theoretical basis on the victory of the undulatory theory. That it was, moreover, empirically untenable was proved by Gladstone and Dale (1858), who also showed at the same time that the similarly formed but simpler function  $(n - 1)\phi$  or  $\frac{n - 1}{d}$  remained much more constant with the temperature, and was therefore to be considered the real measure of the refractive power.

When this formula was tested by Landolt and others, it proved not to give quite constant values, although the approximation was tolerably good. No theoretical foundation for it was proposed.

A new formula met a short time ago with a favourable reception, especially on account of its validity in a case which was in conflict with the previous formulæ. It was deduced theoretically by two

independent physicists, L. Lorenz and H. Lorentz, from different assumptions which need not be here specified, and has the form  $\frac{n^2 - 1}{n^2 + 2}\phi$ .

The values calculated from it are very constant both for the liquid and gaseous states.

A few numbers are collected in the following table—

	Liquid (20).	Gaseous.
Ethyl ether . . . . .	·3029	·3068
Ethyl alcohol . . . . .	·2807	·2825
Water . . . . .	·2061	·2068
Chloroform . . . . .	·1791	·1796
Ethyl iodide . . . . .	·1558	·1571
Ethyl acetate . . . . .	·2549	·2683
Carbon disulphide . . . . .	·2809	·2898

In spite of the enormous change of density the agreement is excellent. The older formula  $(n - 1)\phi$  is in this case inapplicable, giving much more divergent numbers.

In other cases, however, the older formula is superior to the new one. If the density of the liquid is altered by pressure and the refractive indices then determined, the expression  $(n - 1)\phi$  appears much more constant than  $\frac{n^2 - 1}{n^2 + 2}\phi$ . The same holds for alteration of density by temperature and for the case of mixtures.

If there is a value  $r$  for the optical properties which is independent of the physical state of the substance, the value  $r$  of a mixture must evidently be equal to the sum of the values of the components. If we have therefore two substances whose optical properties,  $(n - 1)\phi$  or  $\frac{n^2 - 1}{n^2 + 2}\phi$ , are equal to  $r_1$  and  $r_2$ , and mix  $m_1$  parts of the former with  $m_2$  of the latter, then

$$m_1 r_1 + m_2 r_2 = (m_1 + m_2) r,$$

or

$$r = \frac{m_1}{m_1 + m_2} r_1 + \frac{m_2}{m_1 + m_2} r_2.$$

This relation, as Landolt and Wüllner have shown, is fulfilled with close approximation by the function  $r = (n - 1)\phi$ . The divergence with the new formula is mostly larger.

While the latter therefore gives constant values, notwithstanding the great change in the passage from the liquid to the gaseous state, where the older one fails, yet it yields worse results for the relatively slight alterations caused by pressure, temperature, and mixing.

It consequently remains uncertain to which of the formulæ the preference should be given for our purpose. However, this is at present of little importance, as the general relations are exhibited in quite the same form by both, only with different numerical values. The old formula has simplicity to recommend it, but the "theoretical" one has been almost exclusively used in recent years. Both will be employed in what follows.

When the refractive constant of a mixture had been shown to be the sum of those of the components, each multiplied by the proportion of the substance in the mixture, the question was not long in being asked, if such a relation did not also exist for chemical compounds. Landolt (1864), who first raised this question, came to the conclusion that the constant of a chemical compound was the sum of the corresponding values of its elements. If  $m$  is the molecular weight of the compound and  $r$  its refractive constant, whether  $(n-1)\phi$  or  $\frac{n^2-1}{n^2+2}\phi$ , and if the constants of the elements are  $r_1, r_2, r_3$ , etc., and their atomic weights  $m_1, m_2, m_3$ , etc., then the relation

$$mr = n_1 m_1 r_1 + n_2 m_2 r_2 + n_3 m_3 r_3 + \dots$$

will hold,  $n_1, n_2$ , etc., being the number of atoms of the respective elements in the compound.

The quantities  $m_1 r_1, m_2 r_2, \dots$ , are called the atomic refractive powers of the elements;  $mr$  is the molecular refractive power of the compound, which is therefore equal to the sum of the atomic refractive powers of the elements. This proposition, like the similar one for molecular volumes, only holds under certain restrictions.

First we have the question of the wave length, to which measurements are to be referred. The dispersion is very different for different substances, and we therefore get results which vary considerably according as the light used is of greater or less wave length. Schrauf (1862) proposed to use instead of any definite wave length the constant

$A$  of the dispersion formula of Cauchy  $n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \dots$ , where  $\lambda$

is the wave length, and in which for  $\lambda = \infty$  the index of refraction  $n = A$ , and the proposal was in many cases accepted. It seemed indeed rational to reckon with the index of refraction for infinitely long waves instead of that for any definite wave length. But it turned out that the formula by no means satisfactorily represented the dispersion; according to the observations employed, different values were obtained for  $A$ , and it has been made probable of late, particularly by measurements in the infra-red spectrum, that there is no limiting value of the index of refraction towards which it converges. The employment of a definite ray has therefore again come into practice, the values being mostly made referable to the red hydrogen line of wave length 656.2.

Researches have been mostly made on organic compounds to obtain relations amongst the optical properties, Landolt having discovered the law that refraction is an additive property with such bodies. In the same domain Brühl (1880) discovered the restrictions under which the law holds.

Gladstone had already drawn attention to the fact that many compounds, especially those of the aromatic series, did not obey the

law of Landolt. On more particular investigation, Brühl found that this is the case with all compounds in the molecules of which modern chemistry assumes the presence of doubly linked carbon atoms. Such substances always possess greater molecular refractive power than that calculated from the atoms, and thus the law of Landolt has to be extended in the same way as Kopp's law for molecular volumes. Together with the additive summation we have the constitutive influence, so that the elements contribute differently to the molecular refraction according to the function which they exercise in their compounds.

This was first investigated in detail for carbon, but other measurements show that it holds for oxygen, nitrogen, sulphur, etc., which have varying valency and modes of combination. The following table is given by Brühl—

Carbon . . . . .	2.18
Hydrogen . . . . .	1.04
Hydroxyl oxygen . . . . .	1.58
Carbonyl oxygen . . . . .	2.34
Chlorine . . . . .	6.02
Bromine . . . . .	8.95
Iodine . . . . .	13.99
Nitrogen (single bond) . . . . .	3.02
Double linking of carbon . . . . .	1.78
Triple linking of carbon . . . . .	2.18

The two last values signify that two double-linked carbon atoms do not possess the atomic refraction  $2 \times 2.18 = 4.36$ , but rather  $4.36 + 1.78 = 6.14$ ; in the same way two triple-linked carbon atoms have the refraction equivalent  $4.36 + 2.18 = 6.54$ .

With the help of these constants (which are given with reference to the formula  $\frac{n^2 - 1}{n^2 + 2} \phi$  and the  $\alpha$  hydrogen line) we get molecular refractive powers of compounds which agree very well with those observed. The considerable and very constant influence of double linking has proved several times to be of use in the discussion of questions of constitution. For instance Brühl has pointed out that according to this mode of reckoning, the molecule of benzene has three pairs of double bonds, as Kekulé's formula assumes, but this conclusion has met with some opposition.

We should not assume that the differences between measurement and calculation which still remain are due entirely to errors of observation. In fact it appears from the very extensive material now accumulated that such differences have an actual existence. They are caused in part by our present inability to take dispersion into account, substances with strong dispersion yielding quite regularly a greater molecular refraction than that calculated from the preceding constants. But substances also which have no great dispersive power exhibit similar small deviations, so that the conclusion we

already came to, that constitutive influences are always effecting slight alterations on the additive scheme of the refractive constants, holds in the most general manner. The determination of the nature and amount of these influences still remains the task of the future.

The above constants may be partly tested by calculating the atomic refractions from the refractive indices and densities of the free elements. Thus from the values for gaseous hydrogen and chlorine we get the refractions  $H = 1.05$  and  $Cl = 5.78$ , which agree very well with those obtained from the compounds.

The inorganic compounds have been much less thoroughly investigated than the organic. We owe almost all we know of this subject to the work of Gladstone. Here also we find a general additive law, though it is distinctly modified by constitutive influences. For instance, the molecular refraction of free acids differs from that of their potassium salts by numbers which are very nearly equal in the case of all strong acids; and this, likewise, is the case for weak acids, the differences in the two groups being however unequal. Similarly, when a metal can form several series of salts it appears to have a different atomic refraction in each series.

The determinations of the refractive power of such substances are in general executed on their aqueous solutions. If these consist of  $p$  molecules of water to one molecule of salt, then we have the relation (p. 97)

$$(18p + m)r = 18pr_0 + mR,$$

where 18 is the molecular weight of water,  $m$  that of the salt;  $r$ ,  $r_0$ , and  $R$  the refractive constants  $\left( \text{either } (n-1)\phi \text{ or } \frac{n^2-1}{n^2+2}\phi \right)$  of the solution, the water, and the salt. For the molecular refraction of the salt we thus have

$$mR = (18p + m)r - 18pr_0.$$

By special experiments Gladstone convinced himself that, whether the molecular refraction is determined from the solid salt (he used prisms of rock salt) or from solutions, the result is the same.

## CHAPTER VI

### ROTATION OF THE PLANE OF POLARISATION

THE ability of certain liquid substances to rotate the plane of polarisation of light is of an entirely constitutive character. It is a property possessed by relatively few bodies, which are all, as far as we know, compounds of carbon, and in these it occurs only in connection with certain quite definite circumstances, as we shall see below.

The angle through which the plane of polarisation is rotated by liquids is dependent on their nature as well as on the wave length of the polarised light. It is proportional to the thickness of the layer of liquid passed through, and varies with the temperature.

The angle through which polarised light of definite wave length is turned when it passes through a layer whose thickness is inversely proportional to the specific gravity of the liquid is called the specific rotatory power of that liquid. It is denoted by  $[\alpha]$  and we have the relation

$$[\alpha] = \frac{\alpha}{ld},$$

where  $\alpha$  is the observed angle,  $l$  the thickness of the layer, and  $d$  the density of the liquid. The decimetre is usually employed as the unit of length. If we multiply this value by the molecular weight  $m$ , then  $m[\alpha]$  represents the molecular rotation. As the numbers are very large, the hundredth part of this value is usually taken, so that the

$$\text{molecular rotation } [m] = \frac{m\alpha}{100ld}.$$

If we are working with solutions or mixtures, we may, by making the assumption (in most cases incorrect) that the solvent has no influence on the rotatory power, likewise determine the specific and molecular rotatory power of the substance dissolved. If there are  $p$  grams dissolved in  $v$  c. cm. then we get the specific and molecular rotations

$$[\alpha] = \frac{\alpha v}{lp}, \quad [m] = \frac{m}{100} \cdot \frac{\alpha v}{lp}.$$



If the composition of the solution is given by weight, so that there are  $k$  grams substance in 100 g. solution, and if, further,  $d$  be specific gravity of the solution, its volume is  $\frac{100}{d}$ , so that the expressions assume the form

$$[a] = \frac{100}{kd} \cdot \frac{a}{l} \text{ and } [m] = \frac{ma}{kdl},$$

$l$  being again usually given in decimetres.

The determination of the rotatory power is mostly made for one definite sort of light, almost without exception for the yellow light of the sodium flame; the corresponding values are denoted by  $[a]_D$  and  $[m]_D$ , the sodium line corresponding to the line D in the solar spectrum.

The instruments used in making such measurements cannot be described here in detail. They all consist of two polarisers between which is placed the liquid enclosed in a glass tube shut at the ends by parallel glass plates. If the polarisers are first brought into a definite relative position, say at right angles so that no light passes through, on bringing the tube between them we must turn one of the polarisers through a certain angle to regain the same condition. The different apparatus vary only in the arrangements for identifying and restoring a certain relative position of the polarisers. The angle through which the polariser must be turned is the angle denoted above by  $a$ . Substances are called dextrorotatory when the polariser next the eye (the "analyser") must be turned in the direction of the hands of a watch to restore the previous condition, levorotatory when in the opposite direction.

Whilst with liquid substances the measurement is perfectly definite, considerable difficulties are encountered with substances which must first be dissolved in a suitable liquid. The rotation of the plane of polarisation is a property which shows the most extreme sensibility to external influences, so that quite different values of the specific rotatory power are obtained for one and the same substance when it is measured in different solvents or even in differently concentrated solutions with the same solvent.

This circumstance is at the bottom of our inability to find any undoubted general relations between the molecular rotation and other properties. The theoretical point around which these phenomena turn lies rather in the question, through what circumstances do these bodies obtain their optical activity at all.

The cause of the same property in certain crystalline solids is recognised with great probability in a quite definite arrangement of their ultimate particles. Reusch (1869) first established the fact that an optically active body could be artificially made by piling a number of plates of mica together so that the optical axis of each was turned through a definite angle with respect to that of the preceding plate. A similar spiral arrangement of the smallest particles is to be assumed

in the case of quartz and other optically active crystals, and this assumption is borne out very completely by their crystallographic properties.

The molecules of liquids cannot be so arranged, since they are in continual movement. Any spiral structure must, therefore, be inside the molecules themselves. This is supported by an experiment of Biot's, according to which the vapours of optically active substances still continue to rotate the plane of polarisation.

Now Le Bel and van't Hoff showed almost simultaneously (1874) that all optically active substances that could rotate the plane of polarisation in the non-crystalline state contained an "asymmetric" carbon atom, *i.e.* one whose four valencies were satisfied by four atoms or radicals of different kinds. If we imagine the four valencies at the summits of a tetrahedron, we can arrange the four different radicals on them in two ways, producing forms which can in nowise be superposed. If these four radicals be denoted by *a*, *b*, *c*, *d*, and if the tetrahedra be imagined resting with one face on the plane of the paper, we have the following symmetrical but not superposable figures—

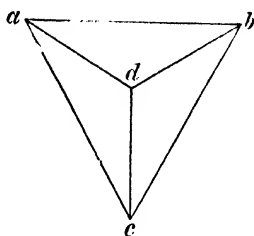


FIG. 9.

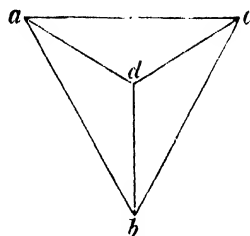


FIG. 10.

If the two tetrahedra are so placed that the radical *d* is at the apex, the order *abc* is in one case clockwise, in the other counter-clockwise.

Whatever we may think of the assumption of the tetrahedral arrangement of the valencies—an assumption which has of late proved very useful in another field—the fact is at least very remarkable, that hitherto no optically active substance has been discovered which does not, in the above sense, possess an asymmetric carbon atom.

It is true, on the other hand, that very many substances are known which contain asymmetric carbon atoms yet do not rotate the plane of polarisation. This circumstance, however, finds a plausible explanation from the same theory. If a substance containing asymmetric carbon atoms is produced in a reaction, there will in general be formed as many molecules with dextrorotatory as with levorotatory carbon groups. We therefore get a mixture in which the one rotation just counterbalances the other, so that the substance will on the whole appear optically inactive. Only when the two opposite portions are separated are we in a position to observe their optical activity.

According to the theory, therefore, every compound with an asymmetric carbon atom ought to exist in two distinct forms, one of which should rotate the plane of polarisation as much in the one sense as the other should in the opposite sense.

Such a relation has in fact already been found in many cases. It was first discovered by Pasteur (1848) with the tartaric acids; the same was afterwards observed with malic acid, mandelic acid, and other substances, so that it is highly probable that the relation holds generally. Accordingly, it must not be conceived as a peculiar property of a substance that it is dextro or levo-rotatory, but rather there must exist for every optically active substance a dextrorotatory as well as a levorotatory modification.

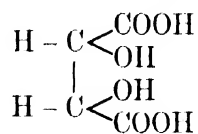
Such optically opposed forms only differ in their optical and crystallographic properties; their whole chemical behaviour is identical in the minutest particular. Only when they react with other also optically active substances can they form compounds with different properties. Equal quantities of both forms, however, when mixed often form actual compounds with each other, and these naturally behave differently from their components.

Ordinary dextrotartaric acid, for instance, has precisely the same properties as levotartaric acid; but the compound of both which crystallises from their mixed solutions on evaporation—racemic acid—has quite a different character. The first named crystallise anhydrous, the last hydrated; the simple acids do not precipitate a solution of calcium sulphate, the compound acid does, and so forth. Yet it should be emphasised that such differences only occur with solid compounds; racemic acid behaves in solution like a mixture of the two components.

In this respect the hypothesis of Le Bel and van't Hoff is thus in the best accordance with known facts. But other circumstances too, observed with the tartaric acids, find a sufficient explanation from the hypothesis.

Along with the two active tartaric acids and racemic acid there exists a fourth acid of the same composition which is optically inactive like racemic acid, but cannot like this be split up into the dextro and levo-acids. It also possesses different chemical properties from racemic acid.

To interpret this fact from the standpoint of the theory we must remember that tartaric acid, corresponding to the formula



has two perfectly similar asymmetric carbon atoms. These may be so constituted that the ray of light is rotated by both in the same sense,

either clockwise or the opposite; this would be the constitution of dextro and lævo-tartaric acids. But on the other hand there may be united with each other two asymmetric carbon atoms with opposite action on the polarised ray. Then, as the constitution of the two asymmetric groups is in this case identical, there will be complete compensation within the molecule itself—the substance is optically inactive and cannot be split up into active components.

Accordingly, such inactive forms can only occur with substances which have an even number of asymmetric carbon atoms similarly constituted in pairs. Experience in this case also has never been in direct contradiction to the theory, for although some observations seem to point to exceptions, yet these have not been sufficiently investigated.

A group of phenomena closely related to the preceding is the magnetic rotation of the plane of polarisation, discovered by Faraday in 1846. Transparent substances brought into a magnetic field or into the interior of a coil of wire conducting an electric current, acquire the power of rotating the plane of polarised light, and retain this as long as the magnetic or electro-magnetic action lasts. The angle of rotation is proportional to the intensity of the magnetic field, to the thickness of the layer of substance through which the light has to pass, and is further dependent on the nature of the substance and the temperature.

The investigation of this subject was first carried out from the physical standpoint. Perkin (1882), to whom we owe almost all our knowledge of it, first considered the matter with reference to chemical composition.

The ratio of the rotations effected in the same magnetic field by the substance in question and by water he calls the specific rotation, the lengths of the two columns of liquid being inversely proportional to their densities. If  $\omega$  be the angle of rotation for a column of the length  $l$  of the substance whose density is  $d$ , and if  $\omega_0$ ,  $l_0$ , and  $d_0$  be the corresponding numbers for water at the same temperature, then the specific rotation  $r = \frac{\omega l_0 d_0}{\omega_0 l d}$ . The molecular rotation is the ratio of the rotations of molecular quantities, and is

$$\rho = \frac{M \omega l_0 d_0}{18 \omega_0 l d} = \frac{M}{18} r,$$

where  $M$  is the molecular weight of the substance, 18 being that of water. The molecular rotation of water is consequently equal to unity.

From a comparison of the molecular rotations of different substances, an additive character in this property was only seen in homologous series; every addition of  $\text{CH}_2$  in such corresponds to an increase of 1.023 units. This value remains the same for all series. The

molecular rotation can thus be represented by  $C + n1.023$ , where  $n$  is the number of  $\text{CH}_2$ -groups and  $C$  is a constant having a special value for each homologous series. These constants are purely constitutive; they are different for normal and iso-hydrocarbons, normal and iso-alcohols and acids. The formulæ too only hold for such compounds as possess at least one methylene,  $\text{CH}_2$ ; for instance the constant .393 of the normal fatty acids does not apply to formic acid,  $\text{HCOOH}$  and acetic acid,  $\text{CH}_3\cdot\text{COOH}$ , in which  $\text{CH}_2$  is not contained.

The magnetic rotatory power has, in virtue of these relations, already proved useful in determining whether a certain substance belongs to this or that group of compounds. General relations between the constants and the constitution of the compounds have not yet been discovered.

## CHAPTER VII

### SURFACE TENSION

THE surface which liquids expose to “free” space, *i.e.* space filled with their own vapours or with other gases, is of a different character from the interior. Whereas every particle has freedom of motion in the interior, a particle lying at the surface can only move in the direction of the liquid; considerable forces oppose its motion out of the liquid. We can easily conceive that this must be so. In the interior of the liquid every particle is equally attracted on all sides, and can therefore move as if no force acted upon it. But if it lies on the surface, the action of the adjacent particles, enclosed by a hemisphere whose radius is the distance at which the molecular forces can still act, has a resultant at right angles to the surface.

The force brought about in this fashion is very great. It can be measured in the way indicated by Stefan (1886). If we imagine a

particle moving from the interior of a liquid towards the surface, half the molecular attraction must be overcome before the surface is reached, as we at once see from Fig. 11. If now the particle pursue its course further into the space above the liquid, it gets finally altogether out of the sphere of attraction

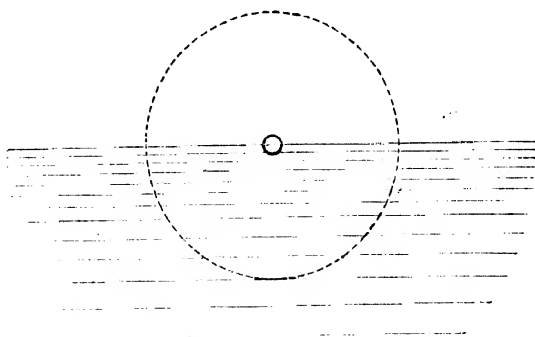


FIG. 11.

of the latter—becomes a particle of vapour. To bring a liquid particle into the surface requires therefore half the work necessary to transform it into vapour. But this work is known; it is the heat of vaporisation of the liquid.

To arrive at a conception of the magnitude of the forces here in play we may make an approximate calculation. If  $v$  is the volume of 1g of the

liquid,  $\Lambda$  its heat of vaporisation,  $p_2$  the (unknown) surface pressure within the liquid and  $p_1$  the vapour pressure, the work necessary to bring the particles into the surface is  $(p_2 - p_1)v$ , if  $v$  may be taken as constant for a first approximation. We have consequently, according to the above,

$$(p_2 - p_1)v = \frac{1}{2}\Lambda.$$

For ether at its boiling-point, for example,  $v = 1.37$ ,  $p_1 = 1$  atm.,  $\Lambda = 86$  cal. To pass from thermal to mechanical measure we must multiply the 86 by 42355; if we divide simultaneously by 1033 to get the pressure in atmospheres it follows, since  $p_1 = 1$ , that the surface pressure  $p_2 = 1284$  atm.

As we see, we have here to do with very large pressures in the interior of the liquid. Of course they are not experienced by immersed bodies, because a liquid surface is formed on these also, the pressure being directed away from the body into the liquid.

A small portion of such pressures acts in the surface of the liquid. For, if the surface of the liquid be increased, we must bring a certain number of internal particles into the superficial layer, and so perform work. Conversely, there will always be in a liquid the tendency for as many molecules as possible to pass into the interior of the liquid consequent on the molecular attraction, whereby the surface is lessened. The surfaces of liquids behave, therefore, as if under the action of a contractile force within them, which strives to reduce them to the smallest possible area.

This conception of the phenomena, deduced from the forces just considered as consequences of a surface tension of liquids, is due to Young (1804), and has proved extremely serviceable. We can, without having to overcome any other than mathematical difficulties, deduce theoretically all the corresponding phenomena, usually called capillary, from the principle that liquids, in consequence of this tension, strive to form the smallest surface compatible with the given conditions.

The difficulties of calculation are, however, even in apparently simple cases, of more than ordinary magnitude.

The surface tension  $\gamma$  is equal to the force which acts on 1 cm. of the boundary line at the surface. The work of forming 1 sq. cm. of surface is numerically equal to this.

To measure the surface tension we almost always make use of solid walls which are wetted by the liquid, *i.e.* walls on which a layer of the liquid will spread. If (Fig. 12) such a wall be dipped perpendicularly into the liquid,

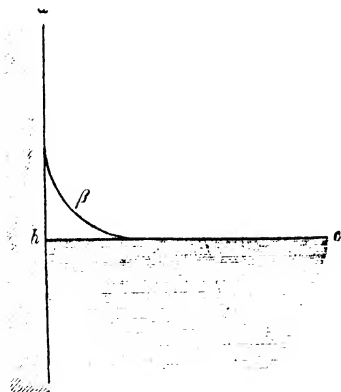


FIG. 12.

the whole surface  $abc$  will strive to become less and will assume the form  $a\beta c$ . A state of equilibrium will be reached when the

weight  $P$  of the liquid raised along the wall is equal to the surface tension  $\gamma l$ , where  $l$  is the length of the line of contact. From  $P = \gamma l$

we get  $\gamma = \frac{P}{l}$ .

If the wall has a cylindrical form, *i.e.* if we have to do with a tube,  $l$  is in this case equal to  $2\pi r$  if the circular section has the radius  $r$ , and the elevating force will be  $2\pi r\gamma$ . The weight raised is, on the other hand,  $P = \pi r^2 h s$ ,  $h$  being the height,  $\pi r^2$  the section ( $\pi r^2 h$  consequently the volume), and  $s$  the specific gravity of the column of liquid.

It follows that  $2\pi r\gamma = \pi r^2 h s$  or  $\gamma = \frac{1}{2} h r s$  and  $h = \frac{2\gamma}{rs}$ . The capillary

height is therefore inversely proportional to the diameter of the tube, and the surface-tension is equal to half the product of the height, the radius of the tube, and the specific gravity of the liquid.

Another method of measuring surface tension consists in determining the weight of the drops of liquid supported by a given circumference. If  $P$  is the weight of the largest drop that can hang from a horizontal plane surface of circular form, and having the radius  $r$ , then  $P = 2\pi r\gamma$  and  $\gamma = \frac{P}{2\pi r}$ . The difficulty of the method lies in the drop not separating as a whole from the surface when it falls off, but always leaving a more or less considerable portion behind. We should weigh the hanging, not the detached drop.

Another method, in principle the same, is to bring a disc of known size into contact with the liquid and then determine the weight necessary just to separate the disc from the liquid. Here again we have the equation  $P = 2\pi r\gamma$ , where  $2\pi r$  is the circumference of the disc, supposed circular.

It is assumed in all these calculations that the solid can be to this extent considered a part of the liquid, that it is in the neighbourhood of the line of contact completely overspread with the liquid, the latter meeting it with continuous curvature. It was first shown by Gauss that the liquid could also meet the solid at a finite angle  $\alpha$ . The force then exercised by the surface tension is smaller and, as a simple geometrical consideration shows, equal to  $\gamma \cos \alpha$ , where  $\alpha$  is the angle between the normal to the solid and that to the last particle of liquid at the line of contact. If the liquid wets the solid wall this angle seems always to vanish, but measurements of its exact size are difficult to make.

The surface tension  $\gamma$  depends on the nature and on the temperature of the liquid. It is very nearly proportional to the temperature, so that in general the surface tension  $\gamma_t$  at the temperature  $t$  can be given by an expression of the form  $\gamma_t = \gamma_0(1 - at)$ . According to this equation there must be a temperature at which  $\gamma_t = 0$ . Frankenheim (1841) pointed out that this temperature probably coincided with the critical point. On the basis of the above considerations regarding the relation between the latent heat of vapours and surface tension the same conclusion is arrived at, for at the critical temperature, when



liquid and vapour become identical, there is no latent heat of vaporisation and consequently no surface tension.

Researches on the connection between surface tension and chemical constitution were first made by Mendelejeff (1866), but these yielded no general result. Schiff in 1884 took the subject in hand and determined, in the first place, the surface tension of sixty organic compounds at their respective boiling-points, thinking to obtain more general relations from this choice of temperature. He further introduced a new constant, the number of molecules elevated above the external surface. As the surface tension  $\gamma$  is equal to the weight raised  $p$  for unit length of the line of contact, then, if  $m$  be the molecular weight,  $\frac{p}{m} = \frac{\gamma}{m}$  is proportional to the number of molecules

raised. Schiff multiplies this magnitude  $\frac{\gamma}{m} = N$  by 1000 in order to obtain convenient numbers. The value of  $N$  proved to be the same for isomeric organic substances. It also remained unchanged when two hydrogen atoms in a compound were substituted for a carbon atom, and conversely. Again, three hydrogen atoms and one oxygen atom, seven hydrogen atoms and one chlorine atom, are in this respect equivalent. It is thus possible to express the composition of every compound by a corresponding multiple of hydrogen, and we find that compounds with the same sum of hydrogen equivalents have equal values for  $N$ . If we denote these sums by  $n$ , the following empirical equation between  $N$  and  $n$  holds good—

$$\log N = 2.8155 - .00728n - \log n.$$

For instance, in the case of propyl chloride,  $C_3H_7Cl$ , the number  $n$  is equal to  $3 \times 2 + 7 \times 1 + 1 \times 7 = 20$ ; calculation gives  $N = 23.4$ , while the observed result is 23.8. The agreement is much the same in other cases.

With reference to the surface tension of salt solutions it may be observed that it varies very nearly proportionally to the quantity of salt present. Solutions of organic substances have a smaller surface tension than that of the solvent (water) alone; the difference is usually considerable, and increases very rapidly as the substances contain more and more carbon.

To give a few numerical examples, the surface tension of water in the neighbourhood of  $0^\circ$  is  $\gamma = .088$  (cm. g.) in gravitation units, *i.e.* for a contact line 1 cm. long .088 g. water is raised. For mercury  $\gamma = .585$ . As the capillary elevation  $h = \frac{2\gamma}{rs}$ , water in a tube of 1 mm. radius rises to the height of 1.76 cm.,  $r$  being .1 and  $s = 1$ . Calculating in the same way for mercury, sp. gr. = 13.59, we get .861, but we have yet to take into account that the angle  $a$  in this case is finite, having a value of about  $130^\circ$ , so that, multiplying by the

cosine of this angle, we obtain a value  $-.55$ , *i.e.* the mercury in the tube is depressed  $.55$  cm. below the level of that in a communicating vessel of large surface.

These data can be used to make an approximate calculation of the size of the molecules. The number  $\gamma = .088$  also measures the work necessary to produce 1 sq. cm. of water surface. On the other hand, the work requisite to bring the molecules of 1 g. water into the surface is equal to half the latent heat of water vapour (p. 107), which at  $0^\circ$  is about 600 cal. The half of this number multiplied by the mechanical equivalent of heat 42355 gives the work of  $127 \times 10^5$  g. cm., which we are seeking. But to form 1 sq. cm. of surface we only require  $.088$  g. cm., consequently we can make from 1 g. water  $1.44 \times 10^8$  sq. cm. of surface and the thickness of this layer, to be put equal to the diameter of a molecule of water, is accordingly  $.7 \times 10^{-8}$  cm. This is of the same order of magnitude as the diameter calculated on p. 66.

## CHAPTER VIII

### INTERNAL FRICTION

WE have hitherto treated liquids as bodies that assume any form. This is in fact the case, but a certain amount of work is required to effect a change in their form, and this is measured by their internal friction. It is, to be sure, in general very small, but there exist some liquids with large values for the internal friction. The greater these values become, the more do the liquids approach the solid state, and there is a continuous passage from substances like warm ether, which is excessively mobile, to those like cobbler's wax, which behaves in most respects like a solid.

Internal friction occurs whenever a liquid moves so as to change its form, *i.e.* when the particles of the liquid change their relative positions. The coefficient of internal friction  $\eta$  is equal to the work required to move two surfaces 1 sq. cm. in size parallel to one another so far in one second as their distance from each other amounts to. For ordinary liquids the value of  $\eta$  is very small, *eg.* for water at medium temperatures it is not more than .011 (cm. g. s.) in absolute units, or about .000013 in gravitation units.

The internal friction of liquids is best determined by allowing them to run out of cylindrical tubes. For this case we have the formula

$\eta = \frac{D\pi r^4}{8lv}$ , where D is the height of the column of liquid, r the radius of the tube, l its length, and v the volume of the liquid that flows out in unit time;  $\pi$  is the number 3.1415 . . . Higher mathematics is required to obtain this formula, so that here we simply state it.

The relations contained in the formula  $\eta = \frac{D\pi r^4}{8lv}$ , that the effluent volume of liquid is proportional to the pressure and to the fourth power of the radius, were found empirically by Hagen (1839) and Poiseuille (1843). This harmony of theory and practice confirms the assumptions made in developing the former; namely, that the internal

friction is proportional to the size of the moving surface, and to its relative speed.

The formula given above is, strictly speaking, only applicable to the case in which all the work done by the pressure serves to overcome the friction. This never actually happens, as the liquid always leaves the tube with a finite velocity, consequently with some kinetic energy. If  $R$  is the part of the work used up by friction, it, plus the kinetic energy with which the liquid leaves the tube, must be equal to the total work. For the volume  $V$  of the liquid entering the tube at a pressure  $P$ , the work has the value  $PV$ , and therefore  $PV = R + L$ ,  $L$  being the kinetic energy. This now is equal to half the product of the mass  $Vs$  ( $s$  = specific gravity) and the square of the velocity, which is equal to  $\frac{V}{tq}$ , where  $t$  is the time and  $q$  the cross section. We therefore get

$$PV = R + \frac{V^3s}{2t^2q^2},$$

and

$$R = PV \left( 1 - \frac{V^2s}{2Pt^2q^2} \right).$$

A correction must still be applied to the numerical factor of this formula. It was calculated on the assumption that all parts of the flowing liquid have the same velocity. But this is not correct; the flow is faster in the middle, slower at the sides. When this difference is taken into account, a process requiring higher mathematics, the result is that instead of the factor 2 in the denominator we must put  $\sqrt{2} = 1.260$ ; the formula remains otherwise unchanged, and as  $R$  is proportional to the coefficient  $\eta$ , we have

$$\eta = \eta_{\text{(observed)}} \left( 1 - \frac{V^2s}{1.26Pt^2q^2} \right)$$

The value of the coefficient of friction deduced from the dimensions of the tube must thus be diminished in proportion to the second member within the brackets,  $P$  being measured in absolute units. As this member is proportional to the square of the velocity, it is best to diminish the speed of outflow as much as possible by using long tubes and small pressures.

As the determination of absolute values for internal friction is very troublesome on account of the difficulty in procuring and measuring perfectly cylindrical capillaries, we usually resort to finding relative values by taking the internal friction of water at 15° as the temperature of experiment, as standard; it is generally measured to 1 or to 100. This mode of proceeding has the great advantage that the constant of the apparatus can be determined once for all with the same degree of accuracy as falls to the measurements themselves, whereas individual absolute measurements are affected with much larger errors. It is left to the further progress of science to ascertain with equal accuracy the absolute values of the unit chosen.

The apparatus of the author sketched in Fig. 13 has proved to be the most convenient form for relative determinations. Its essential

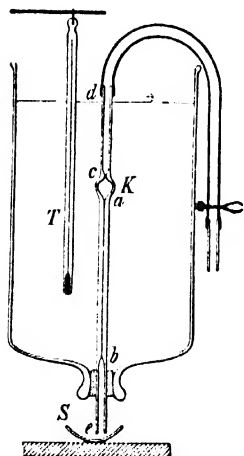


FIG. 13.

parts are a tube *de*, several millimetres wide in its upper portion, which has its bore narrowed at *c* where it passes into a bulb *K*. From the lower end of this bulb proceeds a capillary *ab*, which in its turn is joined to the wider tube *be*. The apparatus is filled to above a mark on the upper tube by sucking, and the time is noted which the surface of the liquid takes to pass from this mark to another beneath the bulb. If *t* is this time for a liquid of specific gravity *s*, and  $\tau$  the time for water, then the relative internal friction  $\rho = \frac{st}{\tau}$ , the pressure in the two cases being as *s* : 1.

A method, formerly much in use, that namely of hanging a circular disc in the liquid by means of a wire and determining the friction from the decrease of the arc of torsional oscillation, is extremely inconvenient. In the first place, we require a comparatively large quantity of liquid. Again, the theory of such oscillations is not completely understood, and the approximations formerly considered sufficient have given errors of as much as 40 per cent with salt solutions; for viscous liquids like rape-seed oil the error mounts to 300 or 400 per cent. Though more recent calculations give results nearer the truth, yet the error they involve is much larger than the error of experiment.

Although several investigators have expended much trouble on the measurement of the friction constants of liquids, no general relation between them and the composition and constitution of the liquids has been found. The first experiments on this subject are those of Graham (1861); later investigations are due to Rellstab (1868) and particularly to Pribram and Handl (1878). The general results are only a few rules applicable to small groups, so that they need not be given here.

In particular nothing has been found that enables us to decide at what temperature the coefficients of friction are comparable. They decrease very rapidly with rising temperature, and a law to represent this change has been recently given by Graetz (1888), but its application has led to no further general results.

Solutions have proved to be somewhat more productive of results, but we cannot here discuss their behaviour.

## CHAPTER IX

### SPECIFIC HEAT OF LIQUIDS

THE definition of specific heat as the quotient of the quantity of heat communicated to unit mass of the substance by the rise of temperature which it effects, has been already given. As the quantity of heat that raises the temperature of 1 g. of water through  $1^{\circ}$  is taken as the unit, the specific heat of water is equal to unity, and that of any other substance can therefore be defined as the ratio of the quantities of heat which must be communicated to equal masses of the substance and of water, or withdrawn from them, in order to bring about the same change of temperature in both cases.

The quantity of heat required to warm a gram of water one degree is not always the same, an increased quantity being necessary as the temperature rises. The exact law of this change is not known, in spite of numerous investigations, for the data given by different observers vary a great deal. It is therefore most convenient to use as unit quantity of heat the hundredth part of the well-determined amount taken up by 1 g. water between  $0^{\circ}$  and  $100^{\circ}$  (or even that quantity itself). This unit is very nearly equal to that obtained by heating water one degree at  $18^{\circ}$ , the mean laboratory temperature. All measurements are in practice referred to the latter unit.

The determination of the specific heat is executed by mixing the substance in question, at the temperature  $t_1$ , and of the weight  $m_1$ , with another liquid, best water, whose temperature and mass are  $t_0$  and  $m_0$ . If there be no external work, as is generally the case, the total heat must remain constant, and we have,  $c_1$  and  $c_0$  being the specific heats and  $t$  the final temperature,

$$c_1 m_1 (t_1 - t) + c_0 m_0 (t_0 - t) = 0,$$

whence

$$c_1 = \frac{c_0 m_0 (t - t_0)}{m_1 (t_1 - t)}.$$

If water is the second liquid  $c_0 = 1$ .

This simple equation is not, however, quite complete. In the first place the liquids are necessarily enclosed in vessels, which likewise take part in the

heating and cooling ; for each of these we must introduce into the equation a corresponding term  $c_n m_n (t_n - t)$ , where  $c_n$  and  $m_n$  must be known ;  $t_n$  is either  $t_1$  or  $t_0$ . Again, a larger or smaller quantity of heat always escapes by radiation, whereby the equation must receive a value other than 0 on the right-hand side. How the last circumstance may be made of no effect cannot be here explained.

The theoretical signification of the specific heat of liquids is rather complicated. The heat communicated serves firstly to increase the energy of motion of the molecules ; secondly for intermolecular work, the molecules moving farther apart with rise of temperature ; and lastly for work within the molecules, the connection of the constituent atoms being altered. We have as yet no means of determining the values of these separate amounts of work, and must therefore fall back upon a purely empirical study of the observations.

In this case, as in so many others, the comparison of observed values is rendered difficult by the temperature having a great and varying influence on the specific heat, which may assume widely different values within comparatively narrow limits of temperature. The researches of Reis (1881) and de Heen (1883) have for this reason yielded no results of a general character.

The experiments of Schiff (1886) led to the unexpected conclusion that regularities in the specific heat of the organic compounds studied were more apparent from a comparison, not of the molecular heats as we might suppose, but of the specific heats for equal weights. It appears that the members of homologous series have specific heats either equal or altering by leaps, and the variation with temperature, expressible by the formula  $k = a + bt$ , has a constant value. Isomerism and molecular weight seem to be without definite influence on the specific heat.

All compound ethers of fatty acids,  $C_n H_{2n} O_2$ , for instance, possess the specific heat  $k = .4416 + .00088t$  ; for the aromatic hydrocarbons from benzene to xylene  $k = .3834 + .001043t$  ; for ethyl benzene, pseudocumene, and mesitylene  $k = .3929 + .001043t$  ; for propyl benzene and cymene  $k = .4000 + .001043t$ .

As the total number of compounds studied is ninety-one, and the errors of experiment are less than a half per cent, the accuracy of Schiff's conclusions can scarcely be doubted. From his data, no regularity can be perceived as to which compounds have the same constant in the formula for the specific heat, and which different constants.

## BOOK IV

### SOLUTIONS

#### CHAPTER I

##### SOLUTIONS OF GASES IN GASES

SOLUTIONS are homogeneous mixtures—mixtures which allow no separation of their components by mechanical means. The ability of gases to form such mixtures is unlimited, that of liquids is limited. Solid substances too can form mixtures which come under the above definition, but not as such, the solutions being produced only when the components have previously united as liquids to a homogeneous mixture, or when they are brought under the influence of great pressure into a condition bordering on the liquid state.

Gases, as aforesaid, mix in all proportions. The properties of the components of such mixtures are preserved unchanged, with the exception of those conditioned by the expansion of each component to the total volume of the mixture. Other exceptions to this rule are only found when the gases are so compressed as to approach the state of liquids.

The general expression for the behaviour of gases is as follows: The pressure of a gaseous mixture is the sum of the partial pressures of its components. We find the partial pressures by imagining each gas separately to fill the total volume and calculating the pressures corresponding.

We might also say that the total volume of a gas is equal to the sum of the volumes of its components, each gas being supposed compressed to its proper volume by the total pressure on the mixture. The first expression is more correct for uniformly mixed gases, the second for stratified gases. As the first case is by far the more frequent, we have practically it alone to consider.

If  $P$  and  $V$  be pressure and volume for a gaseous mixture,  $p_1$ ,  $p_2$ ,



$p_3, \dots$  and  $v_1, v_2, v_3, \dots$  the corresponding values for its component gases, we have the equation

$$PV = p_1v_1 + p_2v_2 + p_3v_3 + \dots,$$

which for a uniform mixture becomes

$$PV = V(p_1 + p_2 + p_3 + \dots),$$

and for superimposed layers

$$PV = P(v_1 + v_2 + v_3 + \dots).$$

If two gases are superimposed they gradually mix. Berthollet made the experiment of inverting a flask full of hydrogen over a similar flask filled with the very much heavier carbonic acid, so that the two openings of the flasks fitted exactly to each other. After a few days carbonic acid was found in the upper flask and hydrogen in the lower, both having moved against the force of gravity. This property of diffusion is shared by all gases. Whenever two masses of gas of different composition are brought into contact, they continue to penetrate into each other until a uniform mixture is formed.

This phenomenon is easily conceivable from the standpoint of the kinetic theory of gases (p. 61). The molecules of the one gas in virtue of their rapid translatory motion soon penetrate amongst those of the other, and so a process of mixture begins, which continues uninterruptedly until it reaches an apparent end after the molecules of each gas present are equally distributed through the whole space. The mixing then ceases only apparently; it actually goes on as before, but it can no longer alter the state of the mixture once this has become uniform.

These phenomena are of great importance with respect to the constitution of the atmosphere. Together with the continual massive motion of currents within it they cause the surprising uniformity of its composition. They have also been of importance in the development of the kinetic theory of gases, for they give us the means, although only through the instrumentality of somewhat difficult and not yet perfectly satisfactory mathematical theories, of calculating the mean free paths of the gas-molecules and consequently also their dimensions (cf. p. 65).

We can get a good notion of the difference of the velocity of diffusion by placing a drop of bromine in the bottom of each of two bottles, one of which contains air and the other hydrogen. The bromine soon becomes converted into vapour, which lies for a pretty long time at the bottom of the bottle containing air, while in spite of the far greater difference of density, it diffuses rapidly upwards in the hydrogen.

## CHAPTER II

### SOLUTIONS OF GASES IN LIQUIDS

THE solubility of gases in liquids, or the capability of both to form homogeneous liquid mixtures, is also as good as general. The solubility of gases in some liquids, however (in mercury for example), is very slight, so that it may as a rule be entirely neglected ; still several facts point to the existence of a certain solubility even in such cases.

The quantity of a gas taken up by a given liquid depends on the nature of both and on the temperature. For the rest it is, as Henry (1803) found, proportional to the pressure of the gas. If we call the quantity of the gas contained in unit volume (both of the liquid and of the space above it) the concentration of the gas, the law may be thus expressed, that under given conditions the ratio of the concentrations in the gas itself and in the liquid remains constant although the pressure varies. This ratio we will call the coefficient of solubility, or simply the solubility of the gas.

A number closely related to this value is what Bunsen (1855) has defined as the coefficient of absorption. This signifies the volume of gas at  $0^{\circ}$  and 76 cm. pressure which is taken up by 1 c. cm. of the liquid at the same pressure, and only differs from the solubility as above defined by the volume of gas being reduced to  $0^{\circ}$ , *i.e.* being divided by  $1 + .00367t$ . It seems more reasonable to give the volume of gas for the temperature at which the solubility itself has been determined ; Bunsen's definition, however, is still very widely spread, and must therefore be mentioned.

The calculation of an absorption experiment in which  $v$  volumes of the liquid has dissolved  $V$  volumes of the gas at  $t^{\circ}$  and  $p$  cm. pressure is made, according to Bunsen, by reducing the gas volume to normal conditions by multiplying by  $\frac{p}{76(1 + \alpha t)}$  ; then the quantity of gas is calculated which would be dissolved according to Henry's Law at the normal pressure through multiplication by  $\frac{76}{p}$  ; and lastly by dividing by  $v$  we obtain the quantity

absorbed by unit volume of the liquid. The coefficient of absorption  $\beta$  is thus equal to  $\frac{V}{v} \cdot \frac{p}{76(1+at)} \cdot \frac{76}{p} = \frac{V}{v(1+at)}$ . The solubility as defined above is simply  $\lambda = \frac{V}{v}$ .

Bunsen and his pupils have determined the absorption coefficients for a great number of gases towards water and alcohol at temperatures between  $0^\circ$  and  $20^\circ$ . The numbers are mostly not large, and vary for the "permanent" gases—nitrogen, hydrogen, oxygen, carbon monoxide, and methane—between .02 and .05. The more easily condensable gases, such as carbon dioxide, nitrogen monoxide, and hydrogen sulphide, have coefficients between 1 and 4. These numbers are for water; for alcohol they are from two to eight times as large, the two series not being proportional.

The solubility usually diminishes with increase of temperature, but Bunsen states that in the case of hydrogen in water, and oxygen or carbon monoxide in alcohol, the coefficient between  $0^\circ$  and  $25^\circ$  is independent of the temperature.

Mixed gases, as Dalton (1807) found, are dissolved according to their partial pressures; the solubility of each component is not influenced by the presence of the other components. The proportion between the gases is in general changed on solution; the fact must be specially emphasised that the final and not the original partial pressures are determinative of the equilibrium.

The accuracy of the above laws is of the same nature as that of the fundamental laws of gases; they are limiting formulæ approached more or less nearly by the actually existing relations, and that in general the better the smaller the solubility is, and the lower the pressure. Yet with even such a soluble gas as carbon dioxide Henry's Law holds up to pressures of 4 atm. with an error of only one per cent.

Henry's Law is in general not applicable to gases of which the volume dissolved amounts to several hundred times the volume of the liquid. However, we have regularly in such cases a chemical action between the gas dissolved and the solvent, the dissolved part being so changed chemically that it does not come directly into play in the final equilibrium. Here the amount dissolved increases much more slowly than the pressure, and the determination of an absorption coefficient becomes impossible. Sometimes at lower temperatures deviations occur which vanish again at higher temperatures when the solubility becomes less. Thus sulphur dioxide follows Henry's Law above  $40^\circ$ , but ceases to obey it below this temperature; ammonia is not dissolved by water according to the law until the temperature reaches  $100^\circ$ .

If we take the solution of a gas saturated under a definite pressure, and then diminish the pressure, the excess of gas does not by any means at once

leave the liquid. Such solutions in fact easily remain "supersaturated," and only part with the excess when they are brought into intimate contact with the gas under the diminished pressure, or better with a foreign gas, in which the partial pressure of the dissolved gas is zero. Thus porous powders containing much air, when introduced into solutions of gases, as well as violent shaking, which distributes numerous tiny gas bubbles in the interior of the liquid, are particularly effective in this respect. On the other hand, supersaturated solutions of gases may be kept for very long periods in glass vessels carefully cleaned (with sulphuric acid, caustic alkali, etc.)

The molecular theory of the solution of a gas in water is very simple. When the gas-molecules reach the surface of the water they are held there in virtue of an attraction between them and the water molecules. When now a certain number of gas-molecules have been taken up, it will happen that one of those already in the liquid will free itself from the attraction of the latter and return into the space containing the gas. This will occur the more frequently the more molecules of the gas there are in the liquid, and finally a state of equilibrium will be reached when just as many molecules leave the liquid as enter it.

If the pressure changes, the number of molecules impinging on the surface of the liquid will change in the same proportion; equilibrium therefore can only exist when the number of the molecules leaving the solvent, or the number of dissolved molecules, alters likewise in this ratio. The quantity of gas dissolved is therefore proportional to the pressure.

For gaseous mixtures equilibrium will be reached with every component according to the number of its molecules, *i.e.* to its partial pressure, independently of the other components, as the number of molecules entering and leaving the liquid will be in each case equal to one another. This is Dalton's Law (p. 120).

Variation of temperature changes the number of the impinging molecules, but also the number of the liberated molecules in the same sense, so that it would be in the first instance without influence. Simultaneously, however, the condition of the liquid changes, and with it the attraction between its molecules and those of the gas, the force of the attraction being lessened by increase of temperature. The decrease of solubility mostly observed with rise of temperature is due to this last circumstance.

If instead of pure water we take solutions of different substances to absorb the gases, we find the solubility of the latter in most cases diminished. Absorbed gases are therefore partially given up by liquids when these are made to dissolve solid substances. In particular cases, *e.g.* those investigated by Raoult (1874) where potash and soda solutions were saturated with ammonia, it appears that the diminution is proportional to the quantity of solid dissolved. Setschenoff (1875) got similar results for various salt-solutions towards carbon dioxide, but besides the action of solution there

was here in some cases the chemical action between the carbonic acid and the base of the salt, so that the whole phenomena became much more complicated. In the simplest cases the total quantity dissolved was composed of a chemically bound portion proportional to the salt present and independent of the pressure, and of another portion simply dissolved and proportional to the pressure. In other cases the first portion showed itself dependent on the pressure but in a much less than proportional degree; here of course there was also a chemical action, but it was incomplete and variable with the pressure.

Evolution of heat in varying quantities is almost without exception attendant on the solution of gases in water.

## CHAPTER III

### SOLUTIONS OF LIQUIDS IN LIQUIDS

THE relations between gases and liquids are much simpler than those of the latter among themselves. In the first place, by no means all liquids are soluble in each other; there are some that are almost without mutual action, although that there is absolutely no action may be doubted. Such liquids dissolve each other in general only partially, A taking up a little of B to form a homogeneous mixture with the essential properties of A, and B at the same time dissolving a quantity of A, the properties of the mixture being essentially those of B. No case is known of a liquid partially soluble in another, which cannot also dissolve some of the latter.

Besides this group of pairs of liquids we have another, the pairs of which mix in all proportions with each other, *e.g.* water and alcohol, chloroform and carbon disulphide. The groups are not sharply separated, for some pairs exist which at certain temperatures are not miscible in all proportions, while at other temperatures they are.

The properties of solutions of liquids in liquids are not in general those which would be calculated from the simple rule of mixing. It is known, for instance, that the volume of a mixture of alcohol and water is not equal to the sum of the volumes of its components, but smaller. If we fill a tube about a metre in length and closed at one end about half full of water and then fill up with alcohol, we see after the liquids have been mixed by inverting the tube a few times that there is an empty space of several centimetres at the top.

Many other properties are affected in the same way. The compressibility, expansibility by heat, surface tension, specific heat, etc., all show values more or less different from those calculated. These deviations are usually especially large when water is one of the components of the mixture; being on the average much smaller for other substances, in particular those of chemically indifferent character. No regularity of any importance has been found in such deviations.

The vaporisation of mixed liquids exhibits relations which may be

grouped similarly to those of the solubility. They are simplest in the case of liquids which only dissolve each other to a very small extent, the total pressure being equal to the sum of the separate pressures of the two liquids at the same temperature. A special case of this is that the vapour pressure of a liquid is the same in an atmosphere of gas as it is in vacuo. The law is not quite exact, as both the sum of the pressures and the vapour pressure in the gas are somewhat smaller than the calculated values.

These are further examples of the general principle that the vapour pressure is determined by the state of the liquid in contact with the vapour. As two immiscible liquids are in general still soluble in each other in traces, we have actually not the vapour pressure of the pure liquids but of those which have dissolved some of the other liquid or of the gas in which they stand. Now it is always the case that the vapour pressure of a liquid becomes smaller when it contains a substance dissolved in it, and so we see that the above law holds only for the extreme case of perfect insolubility, and that the actual vapour pressures will always be smaller than those calculated.

If such immiscible liquids are distilled they will go over in a constant proportion for any one temperature, no matter what the composition of the liquid may be, for the vapour consists of the vapours of the components in the ratio of their vapour pressures. As the quantities of the liquids in the receiver are to each other as the products of vapour pressure and density, or of vapour pressure and molecular weight, we can find the molecular weight if the vapour pressure is known.

As a rule, however, we do not know the vapour pressure. It can be found if the relation between the vapour pressure and temperature of the other liquid is known, and the temperature of common ebullition measured. This lies naturally below the boiling-point of the lower-boiling liquid, namely at the temperature at which the sum of the partial pressures of both vapours is equal to the atmospheric pressure. We have only, therefore, to deduct from the atmospheric pressure the vapour pressure of the second liquid at the common boiling-point to get the required partial pressure of the first substance at the same temperature. This method is, to be sure, not very exact. According to Naumann (1877) a mixture of water and nitro-benzene boils at  $99.0^{\circ}$ ; as the vapour pressure of water at this temperature is 73.3 cm., the partial pressure of the nitro-benzene is  $76.0 - 73.3 = 2.7$  cm.

Similar but not quite so simple laws hold good when the liquids are sensibly but still only partially miscible. By shaking up such liquids together, *e.g.* water and ether, we get two layers; in one of which the one liquid preponderates, in the other, the other. They stand in an equilibrium independent of their relative quantities. By using the conception of concentration (p. 119) we can define the state as we did in the case of gases: Equilibrium is attained, when a

definite ratio of concentration is established between the liquids; the absolute and relative quantities of the solutions have nothing to do with the matter.

Two such solutions, in equilibrium on contact and not further miscible, are also in equilibrium with respect to any process by which their concentration might be altered, in particular with respect to their vaporisation. The pressure and the ratio of the components of the vapours given off by the two solutions are exactly equal. The proof of this was given by Konowaloff (1881) both by direct measurement and from theory.

Imagine the two solutions enclosed in ring-shaped space, one above the other; then if *a*, for example, had a greater vapour pressure than *b*, distillation from *a* to *b* through *c* would occur. This would change the concentration of the solution *b*, and the substance in excess would, in order to restore the contact equilibrium, be again taken up by *a* to evaporate from it anew. We could thus obtain a form of the perpetual motion, which, as we know, is impossible.

As each of the two immiscible solutions has thus the same vapour pressure as the other, their common vapour pressure is also independent of the quantity of each. It will be smaller than the sum of the vapour pressures of the separate liquids, as each of these has dissolved somewhat of the other, and thus had its vapour pressure lowered. On distillation a liquid of constant composition passes over, as both solutions give off vapour of the same composition until one or other has all gone over. In the distillate the two components usually separate into two saturated solutions, their ratio being constant on account of the constant composition of the vapour.

The most complicated case is when the liquids dissolve each other in all proportions. Then the liquid is continually changing its composition during vaporisation, which entails a change in the pressure and the composition of the vapour in its turn. If the two liquids have very different vapour pressures and their boiling-points correspondingly wide apart, the vapour pressure and boiling-point of the mixture usually falls between those of the components. The more volatile liquid goes over principally at first during the distillation, the less volatile remaining behind, so that by repetition of the process they may be more or less completely separated.

On the other hand, if the vapour pressures and boiling-points of the components lie near together, two things may happen. Either the mixture behaves similarly to one of liquids not completely miscible, and the vapour pressure of the solution is greater than that of each

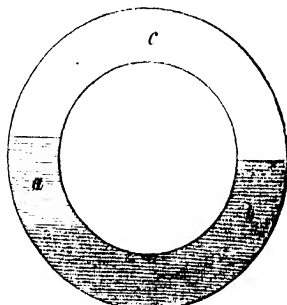


FIG. 14.



component. In this case there must be a certain ratio between the two pure liquids at which the common vapour pressure will attain its highest value. This mixture has consequently the lowest boiling-point of any possible combination, and will on distillation go over first, behaving very like a pure substance with constant boiling-point. In the retort we have left the substance which is in excess with respect to this constant-boiling mixture.

Or again, the mixture of the two liquids may have a lower vapour pressure than either separately. Such liquids must again form in definite proportions a mixture that has the lowest vapour pressure and the highest boiling-point of any. On distilling any mixture of the two anything more volatile passes over first, so that there remains in the retort the mixture with the highest boiling-point, which again behaves almost as a simple substance, distilling unchanged.

In both of these cases the mixture cannot be separated into its components by distillation, but only into another mixture of constant composition and the liquid which is present in excess of this. These constant boiling mixtures have been often erroneously held as simple liquids or chemical compounds, especially when the proportions were nearly molecular. The proportions, however, change continuously with the pressure at which the distillation is performed, so that the assumption of chemical combination of the liquids is excluded. Determinations of the vapour density also show in such cases that the vapours exist uncombined alongside each other.

## CHAPTER IV

### OSMOTIC PRESSURE

WHEN a layer of pure water is brought over any aqueous solution, say one of sugar, the system does not remain in this condition. As in the case of layers of different gases, the sugar at once begins to rise against gravity and to diffuse into the water, the motion only ceasing when the substance is uniformly distributed throughout the whole mass of water.

This motion may be arrested by bringing between the solution and the pure solvent a septum which will let the latter pass but not the dissolved substance. Such a "semi-permeable" wall can be prepared by saturating a porous earthenware cell first with a solution of copper sulphate, rinsing it carefully out, and then filling up with a solution of potassium ferrocyanide. On and within the earthen wall there is formed a continuous sheet of copper ferrocyanide through which water can be filtered. If we try to filter a sugar solution it requires a much greater pressure, and what passes through is not sugar solution but pure water.

Instead of the precipitate of copper ferrocyanide we may employ many other amorphous substances with the same effect, *e.g.* ferric oxide, silicic acid, tannate of gelatine, and the like. The protoplasm of organic cells is generally clothed with a pellicle which has the same property as such artificially prepared membranes.

If such a prepared cell is filled with sugar solution, and then closed by a stopper which admits of connecting it with a manometer, we observe an increase of pressure in the interior of the cell to a definite maximum when it is placed in pure water. The maximum value is dependent on the concentration of the sugar solution and on the temperature.

If the temperature is kept constant, then the pressure is proportional to the strength of the solution (Pfeffer, 1877). The final pressures are very considerable; a one-per-cent solution of sugar

giving 50 cm. of mercury, and a one-per-cent solution of potassium nitrate a pressure of more than 3 atm.

The proportionality between concentration and pressure is seen from the following measurements by Pfeffer on sugar solutions—

Concentration.	Pressure.	Ratio.
1 per cent	53.5 cm.	53.5
2     "	101.6   "	50.8
2.74   "	151.8   "	55.4
4     "	208.2   "	52.1
6     "	307.5   "	51.3

The law that regulates the osmotic pressure has exactly the same form as Boyle's Law, for the pressure exercised by gases is proportional to their density or concentration. It has been shown by many other measurements, both direct and indirect, that the law of osmotic pressure holds for all dissolved substances no matter what their nature.

From this fact, that the particles of a substance in solution exercise a pressure on the neighbouring pure solvent, the above-mentioned phenomenon of diffusion becomes comprehensible. The particles are driven by this pressure into the solvent, and as the pressure is proportional to the concentration, the action will only cease when the same concentration has everywhere been reached.

The extreme slowness with which the diffusion takes place, notwithstanding the magnitude of the pressures, is remarkable. The cause of this is to be found in the friction which the particles experience in moving through the liquid, and in the very small size of the particles themselves. If we reduce a stone, which would fall several hundred feet in a few seconds, to a very fine powder, this will remain under similar circumstances suspended in the air for hours, although gravitation acts upon it with exactly the same force as before. When, therefore, we consider the extraordinary minuteness of the molecules we begin to understand why such very slow progress is made in spite of the great pressures at work.

Temperature has the same influence on osmotic as on gaseous pressure: The pressure increases proportionally to the temperature, and in the same ratio for all dissolved substances. Moreover, this ratio, or the coefficient of tension, has the same value as in the case of gases.

Thus, if we know the osmotic pressure  $P_0$  at  $0^\circ$ , it will be at  $t^\circ$  equal to  $P_0(1 + .00367t)$ . The relation may therefore be expressed in the same way as for gases. The osmotic pressure is proportional to the absolute temperature. In proof of this important relation I give the following measurements by Pfeffer and the corresponding values calculated by van't Hoff—

	Pressure.	At	At	Observed.	Calculated.
Cane sugar	54.4	32°	14.15°	51.0	51.2
"	56.7	36°	15.5°	52.1	52.9
Sodium tartrate	156.4	36.6°	13.3°	143.2	144.3
"	98.3	37.0°	13.3°	90.8	90.7

The values were calculated on the assumption that the coefficient is .00367. The differences are not greater than might arise from errors of experiment.

From experiments with living cells it has been also proved that solutions that are in osmotic equilibrium with the cell contents at 0° remain so at 34°. The increase of pressure was shown in this way to be always the same, however different the solutions employed might be, and however complex the cell contents.

We can thus represent the osmotic pressure of substances in solution by the same general formula as we employed for gases, viz.  $pv = RT$ . The question now arises, what value the constant  $R$  will have in the case of solutions, it being always the same for molecular quantities of different gases. We best calculate it in the latter case for gram molecular weights. At 0° we have  $p = 1033$ ,  $v = 22380$ ,  $T = 273$ , and therefore  $R = \frac{pv}{T} = 84700$ .\*

Now Pfeffer found the pressure to be 49.3 cm. of mercury for a one-per cent sugar solution at 0°. The molecular weight of sugar,  $C_{12}H_{22}O_{11}$ , is 342; the volume in which 342 g. of sugar are contained is therefore 34200 c. cm. The pressure of 49.3 g. of mercury is equal to  $49.3 \times 13.59 = 671$  g. per sq. cm. The temperature 0° C. is 273 in the absolute scale. For sugar the constant is therefore  $R = \frac{671 \times 34200}{273}$

$= 84200$ . As we see, this agrees within the limits of experimental error with the gas constant.

Consequently, the osmotic pressure of a sugar solution has the same value as the pressure that the sugar would exercise if it were contained as a gas in the same volume as is occupied by the solution.

The gas equation  $pv = RT$  holds unchanged with the same constant for solutions, only that  $p$  here denotes the osmotic pressure. For this excessively important principle we have to thank J. H. van't Hoff.

The question, if this be the same for other temperatures and concentrations, must be at once answered in the affirmative, as the applicability of the laws of Boyle and Gay-Lussac to solutions has been already proved. We have only now to ask if Avogadro's law holds for solutions, i.e. if all other substances besides sugar exhibit the same value for  $R$  when molecular quantities are considered. The answer in this case also is affirmative. It is true that there are very few direct measurements of osmotic pressure, but it has been established by the method with organic cells, already indicated, that solutions of the most diverse substances have the same influence, if these substances be contained in the solutions in the ratio of their molecular weight.

\* The last places are here and in what follows rounded off so far as they are rendered doubtful by the error in the experimental numbers.

All the comprehensive relations previously developed as to the connection between vapour density and molecular weight are thus found applicable to solutions, so we may say in general that the state of substances in solution is in the widest sense comparable to that of gases.

Certain groups of substances, in particular salts, together with many acids and bases, show variations from these simple relations. The osmotic pressure they exercise is much larger than it ought to be from their molecular weight; for potassium chloride it is almost twice as large.

Quite a similar irregularity, it will be remembered, appeared in certain definite cases (ammonium salts, etc.) with the vapour density, *i.e.* the pressure was found to be much greater than it ought to have been according to theory. The abnormalities were there explained by admitting the substances to be dissociated, *i.e.* to have split up into simpler molecules. The number of molecules was thus actually much larger than that which corresponded to the formula of the undecomposed substance, and therefore the pressure was greater in the same ratio.

It is natural to assume a similar explanation here—to look upon the substances which exhibit similar abnormalities as being likewise dissociated in their solutions. It will be shown later that this assumption is really well founded, and explains not only this phenomenon but a great many others.

## CHAPTER V

### VAPOUR PRESSURE OF SOLUTIONS

It has already been stated (p. 124) that the vapour pressure of liquids which contain substances dissolved in them is smaller than that of the pure liquid. The laws of this phenomenon, in the first instance for solutions of non volatile substances, were ascertained by Babo (1848) and Wüllner (1856). They are to this effect, that the lowering of vapour pressure is proportional to the amount of substance dissolved, and that for one and the same solution, the lowering at any temperature always remains the same fraction of the vapour pressure of the pure liquid at that temperature.

If we thus denote by  $f$  the vapour pressure of the solvent, that of the solution by  $f'$ , and by  $g$  the amount per cent of the dissolved substance in the solution, we have

$$\frac{f - f'}{f} = kg,$$

where  $k$  is a constant which represents the relative lowering of the vapour pressure for a one-per-cent solution.

This law, however, like so many other such, is only an ideal law, to which the actual relations approximate more nearly the more dilute the solutions become. In concentrated solutions we have deviations, corresponding to those of gases at high pressures, and susceptible of a similar explanation.

If we refer the constant  $k$ , or the relative lowering of vapour pressure, not to equal weights but to molecular weights, we at once find an additional general law, the products of the relative decrease and the molecular weight being constant for one and the same solvent. Thus, if we dissolve in equal quantities of a liquid such amounts of different substances as are proportional to their molecular weights we obtain liquids with the same vapour pressure. The rule may be stated thus: The molecular lowering of vapour pressure produced by all substances in the same solvent is constant.

If, lastly, we compare the relative lowering experienced by different solvents, we find them to be equal when equal amounts of a substance are dissolved in quantities of the various solvents proportional to their molecular weights. Here the vapour pressure of the solution is to that of the pure solvent as the number of molecules of the solvent is to the total number in the solution.

Now, if  $P$  be the weight of the solvent,  $p$  that of the dissolved substance,  $M$  and  $m$  being the corresponding molecular weights, then  $\frac{P}{M} = N$  and  $\frac{p}{m} = n$  are the relative numbers of the molecules. If further  $f$  and  $f'$  represent as above the vapour pressure of pure solvent and of the solution respectively, we have, from what has been already stated,

$$\frac{f'}{f} = \frac{N}{N + n},$$

which can be transformed into

$$\frac{f - f'}{f} = \frac{n}{N + n}.$$

The relative lowering of vapour pressure of any solution is equal to the ratio of the number of molecules of the dissolved substance to the total number of molecules in the solution.

By using the equations  $\frac{P}{M} = N$  and  $\frac{p}{m} = n$  we have finally

$$\frac{f - f'}{f} = \frac{pM}{pM + Pm}.$$

The preceding rules were mostly discovered empirically by F. M. Raoult (1887). They may evidently be used to determine unknown molecular weights of substances, so that we have in them the basis of a much more general method than that of vapour density, many more substances being soluble in volatile liquids, than themselves volatilise undecomposed.

The practical determination of the lowering of vapour pressure is made according to the general methods of ascertaining the vapour pressure. The solution may be introduced into a barometer and its vapour pressure be read off at once from the depression of the mercury column. The vapour pressures of the solvents themselves are for the more common substances already tabulated, but it is more to the purpose to make a second experiment with the pure solvent simultaneously with the other, whereby the effect of any error in the determination of the temperature is eliminated. Attention must be given to the thorough wetting by the solution of the walls of the space in which the vapour is contained, as superficial differences of concentration in thin films readily appear, and this may have a great effect on the readings.

Another method consists in heating in the vapour of the boiling solvent a shortened barometer-tube containing the solution, and conveniently of the form of an inverted siphon. The elevation of the mercury in the closed limb, in which the solution is contained, is then equal to the lowering of the vapour pressure  $f - f'$ , and the vapour pressure of the solvent is equal to the height of the barometer at the time of experiment.

Again, we may determine the boiling-point of the solution under atmospheric pressure. If we know the vapour pressure of the solvent at the same temperature we have all the data required.

Other methods are based upon the determination of the weight of vapour which occupies the same volume at the same temperature, at the pressure of the pure solvent on the one hand, and of the solution on the other. A flask is exhausted and the vapour of weighed quantities of the solvent or of the solution admitted. The quantities that evaporate are proportional to the vapour pressures, the ratio of which can therefore be determined from the respective losses of weight.

In many cases we can make use of the principle that the vapour pressure is the same in gases as in vacuo. If, for instance, a current of air be passed through the solution and then through the solvent, the loss of weight of the first will be to that of the second as  $f' : f - f'$ , the air being saturated with the vapour up to the pressure  $f'$  by passing through the solution, and then further up to  $f$  by passing through the solvent. If in addition we determine the weight of the vapour carried over, this is proportional to the vapour pressure  $f$ .

If we are working with aqueous solutions, the methods of hygrometry may be employed to determine the relative humidity  $\frac{f'}{f}$ .

As to the general validity of the above law, we find that there are here exactly such exceptions as we met with in the case of osmotic pressure. All substances that gave too high values of the latter, and for which therefore a state of dissociation was assumed, exhibit quite the same abnormality with respect to the lowering of vapour pressure. The ratio between the actual and theoretical values of the osmotic pressure is equal to the ratio between those of the lowering of vapour pressure. This circumstance strongly supports the assumption that the cause of the abnormalities lies in the dissolved substance and not, as might also be, in the solvent.

In view of this complete parallelism between the two series of phenomena—osmotic pressure and the lowering of vapour pressure—we must ask if there is no theoretical connection between them. Such a connection actually exists; so that if the laws of osmotic pressure are given we can deduce those of the lowering of vapour pressure from them, and *vice versa*.

We imagine a vessel of the form of an inverted funnel (Fig. 15) which is closed at the bottom by a semi-permeable wall. Let it be filled with the solution L and stand in a vessel F containing the pure solvent. Let the whole now be covered with a bell-jar, and the air be exhausted from this.



The solution will be in equilibrium with the external liquid when the pressure exerted by the column  $hG$  is equal to the osmotic pressure. Now the liquid at  $G$  and the solution at  $h$  are both evaporating; the vapour pressure of the solution at  $h$  must therefore be equal to the pressure possessed by the vapour of the liquid at the same place. For, were it greater or less, liquid would either be deposited or would evaporate at  $h$ ; in both cases the pressure on the semi-permeable wall would change and liquid either enter or leave the funnel. This would go on for ever, so that we could obtain the perpetual motion, which is impossible.

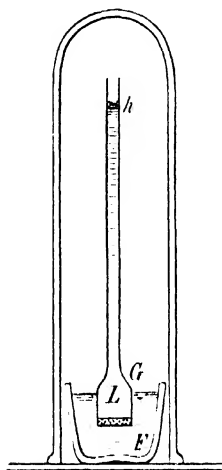


FIG. 15.

The pressure exerted by the vapour of the liquid  $F$  at  $h$  is equal to the vapour pressure of the solvent diminished by the weight of a column of vapour of the height  $Gh$ . To this pressure the vapour pressure of the solution must be equal.

We shall now suppose the laws of osmotic pressure to be given. Let the solution contain  $n$  molecules of the dissolved substance and  $N$  molecules of the solvent. The osmotic pressure is numerically equal to the pressure the substance would exert if it occupied the given space as a gas, *i.e.* by the equation  $pv = nRT$ , whence  $p = \frac{nRT}{v}$ , where  $R = 84700$  (p. 129) and  $T$  is the absolute temperature. To find  $v$ , let us consider that the  $N$  molecules of the solvent weigh  $MN$ , where  $M$  is the molecular weight, and occupy the volume  $\frac{MN}{s}$ , the specific gravity

of the solvent being represented by  $s$ . We thus obtain  $p = \frac{nRTs}{MN}$ . The height  $h$  of the solution corresponding to this pressure is given by the equation  $p = hs'$ , where  $s'$  is the specific gravity of the solution. Let us imagine the solution to be so dilute that its specific gravity does not differ appreciably from that of the solvent, so that we may put  $s' = s$ . Then we have  $h = \frac{nRT}{MN}$ . Since  $MN$  is equal to the weight of solvent that contains  $n$  molecular weights\* of the substance dissolved, we can state the rule: The osmotic elevation is for the same composition by weight independent of the nature of the solvent.

The vapour pressure  $f'$  of the solution is less than that  $f$  of the solvent by the pressure exerted by a column of vapour having the height  $h$ , *i.e.*  $f' = f - hd$ , if  $d$  denote the vapour density. This may also be calculated from the equation  $pv = RT$ ;  $p$ , the pressure of the

\* All weights are to be calculated in grams, here as elsewhere in this book.

vapour, is equal to  $f$ , and  $d = \frac{M}{v}$  as the formula holds for one molecular weight of vapour. Therefore  $d = \frac{fM}{RT}$ .

If we now introduce into the equation  $f' = f - hd$  the values  $h = \frac{nRT}{MN}$  and  $d = \frac{fM}{RT}$ , it follows that  $f' = f \left(1 - \frac{n}{N}\right)$  or  $\frac{f - f'}{f} = \frac{n}{N}$ . As the result of the experiments by Raoult we found (p. 132) the formula  $\frac{f - f'}{f} = \frac{n}{M + n}$ . The difference arises from these experiments being made with solutions of finite concentration, while the calculations only hold for infinitely small concentrations; if  $n$  is very small compared with  $N$ , both formulæ give the same result.

## CHAPTER VI

### THE FREEZING-POINT OF SOLUTIONS

A HUNDRED years ago J. Blagden (1788), in a research unusually exact for that age, found between the temperatures at which salt-solutions solidify and the strength of these solutions, the simple relation that they are proportional. His work, however, fell completely into oblivion. Rüdorff in 1861 rediscovered the same fact, and in 1871 de Coppet, who confirmed this result, added the rule that different substances of analogous nature depressed the freezing-point by the same amount if they were dissolved in water in the proportion of their molecular weights.

The further development of our knowledge of this subject was for a long time arrested by the investigation being confined exclusively to water as the solvent, and salts as the experimental substances.

Only when F. M. Raoult studied, in the first instance (1882), aqueous solutions of indifferent organic substances, was the simple law ascertained that equimolecular\* solutions have the same point of solidification. When other substances were then employed as solvents the same result was found, so that the following general formula may be given.

If  $\Delta$  be the depression of the freezing-point of the solvent caused by the solution of  $n$  molecular weights of the substance in  $g$  grams of the solvent, we have

$$\Delta = r \frac{n}{g},$$

where  $r$  is a constant, which depends only on the nature of the solvent. If the molecular weight of the substance is not known, it can easily be ascertained by determining the depression when  $p$  grams of it are dissolved in  $g$  grams of the solvent. We have then  $n = \frac{p}{m}$ , so that the

\* By equimolecular solutions we mean such as contain, in the same quantity of the solvent, quantities of the dissolved substances proportional to their molecular weights.

equation becomes  $\Delta = \frac{r\phi}{mg}$ , or

$$m = \frac{r\phi}{\Delta g},$$

from which we get the molecular weight.

The constant  $r$ , which as we saw above is dependent on the nature of the solvent, may be determined by dissolving substances of known molecular weight in the liquid and observing the depression. Introducing the values so obtained into the first formula,

$$\text{we get } r = \frac{\Delta g}{n}.$$

This law also holds in the first instance only for indifferent substances; salts, strong acids, and bases are exceptional in their behaviour. These exceptions, however, are again closely related to those noted in the case of osmotic pressure and the lowering of vapour pressure; the depressions actually observed are greater than those calculated, and the ratios between the observed and calculated values are the same for the various substances as those found by the other methods.

The apparatus of Beckmann (1888), sketched in Fig. 16, is the best for the practical determination of the depression of the freezing-point. The glass tube *A* contains a thermometer *D* divided into hundredths of a degree, and a stirring rod made of stout platinum wire. A weighed quantity of the solvent is introduced into *A*, which is then placed into a somewhat wider tube *B*, used to form an air-jacket between *A* and the wide outer vessel *C*, into the lid of which *A* is fixed. This external glass vessel contains water or a freezing mixture, the temperature of which lies from 2° to 5° below the freezing-point of the liquid. The thermometer is now observed while the liquid is kept constantly stirred, small clippings of platinum being introduced into *A* to aid in the thorough mixing. At first in consequence of overcooling it sinks below the freezing-point, thereupon suddenly to rise to the correct temperature when the solid substance separates. The freezing-point of the solvent being in this way exactly determined, a known quantity of the

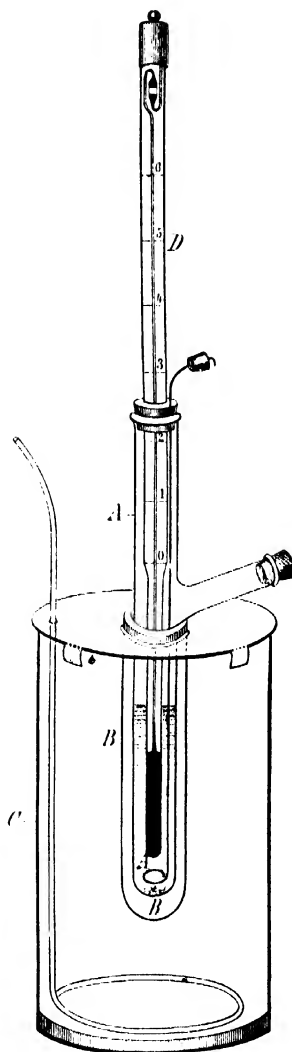


FIG. 16.

substance to be investigated is introduced from a weighed vessel through the side tube into A, the liquid is thoroughly stirred and the experiment repeated. The freezing now takes place at a lower temperature, and the difference of the two temperatures is  $\Delta$  in the equations.

With somewhat concentrated solutions there is often a very strong overcooling, so that on solidification a large quantity of ice\* separates. The solution still remaining is thus too concentrated, and the observed temperature too low. Most of the ice is then allowed to melt, and when only a small quantity is left the apparatus is again brought into the cooled outer vessel.

It is natural to expect between the phenomena of the depression of the freezing-point and the lowering of vapour pressure some such theoretical connection as we found between the latter and the osmotic pressure. The connection in fact exists, and was deduced theoretically by C. M. Guldberg (1870). Van't Hoff (1886) completed the theory in several important points, and showed how to derive the constant  $r$  from other magnitudes.

First of all we must find an answer to the question whether pure ice is deposited or if the solution freezes as a whole. From the experiments made on this subject and the discussion arising from them it appears that the former alternative is the correct one. As long as the solution is not so concentrated that the dissolved substance crystallises out owing to the lowering of temperature, pure ice alone separates.

Now the same mode of reasoning as we employed on p. 125 shows that the temperature at which ice can separate from the solution is that at which ice and the solution have the same vapour pressure. In Fig. 17, *b* now represents the solution, *a* ice, and *c* the vapour. If the ice, for instance, had a greater vapour pressure than the solution it would sublime from *a* to *b*; from the now diluted solution ice would separate at *a*, and the perpetual motion would thus be obtained. The same could also be got if the vapour pressure of *b* were greater than that of *a*. As both these cases, then, are inadmissible, the vapour pressure of the ice and of the solution must be the same.

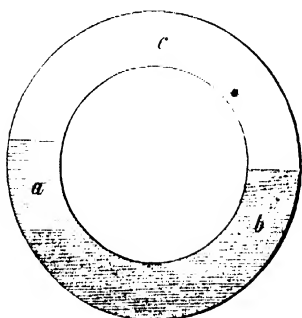


FIG. 17.

From this it follows, therefore, that the laws which we found for the vapour pressure of equimolecular solutions also hold for the depression of the freezing-point.

To render the relations which obtain here quite plain, let *ww* in Fig. 18 represent the curve of vapour pressure for water, the temperatures being the abscissæ and the pressures the ordinates. The curve

\* Ice is here used quite generally for the solidified solvent, be it water, benzene, or any other substance.

for ice *e* has one point (at  $0^\circ$  namely) in common with the curve for water, for if the vapour pressures at the temperature at which ice and water can exist together were different there would be a possibility of obtaining the perpetual motion. Below  $0^\circ$  the ice curve runs beneath the curve for (over-cooled) water. The curve for a solution *ll*, finally, runs below that for water, so that its abscissae always form the same fraction of those of water. The freezing-point of the solution is the abscissa of the point where the curves *e* and *l* cut each other, for both ice and the solution, as we just proved, must have the same vapour pressure.

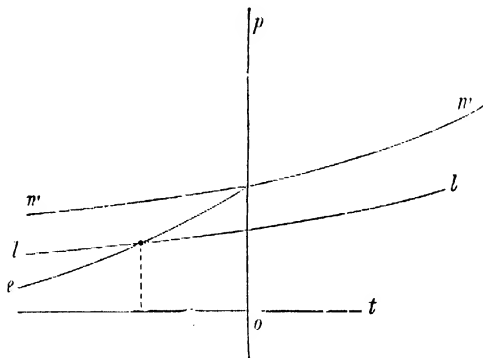


FIG. 18.

The differences of temperature of which we have here to take account are small enough to justify us in considering the corresponding portions of the curves of vapour pressure as straight lines. It is then clear that the point of section of *e* and *l* will move in the same proportion to the left as *l* sinks under *w*. Now this sinking, or the relative lowering of vapour pressure, has been already found both theoretically and experimentally to be proportional to the strength of the solution, and therefore the depression of the freezing-point must be also proportional to the concentration; which is confirmed by experiment, as we have already seen.

The constant *r* may be deduced from the laws of the dynamical theory of heat in the following way. We imagine a large quantity of a solution of *n* gram molecules of substance in *g* grams of solvent enclosed in a cylinder with a semi-permeable wall. By a pressure on the piston a little greater than the osmotic pressure, so much of the solvent is pressed out as corresponds to the volume in which a gram molecule of the substance is dissolved. The work required for this, if *p* be the osmotic pressure and *v* the volume just mentioned, is equal to *p**v*, which in its turn is equal to *RT*. Let this process be performed at the melting-point *T* of the solvent. The quantity of liquid pressed out is  $\frac{g}{n}$  grams.

We now let this quantity of the solvent freeze, when  $\frac{g}{n}w$  calories are evolved if *w* is the latent heat of fusion of the solvent. We then cool everything by  $\Delta$  till the freezing-point of the solution is reached, bring the ice into contact with the solution and let it melt.  $\frac{g}{n}w$  calories are absorbed, but now at the temperature  $T - \Delta$ . Lastly, we warm the whole up to *T* again, so that the system regains its initial state.

Such a process as that just described is called a cycle, and if this satisfies certain conditions (which are here fulfilled) thermo-dynamics teaches us that the work done by heat in this case is equal to the fraction  $\frac{\Delta}{T}$  of the total heat passing from the higher to the lower temperature, where  $\Delta$  is the difference of temperature and  $T$  the absolute temperature of the transformation. In the present case the total heat is  $\frac{g}{n}w$ , so that the portion  $\frac{\Delta gw}{Tn}$  is transformed into work. But this work has been found equal to  $pv$  or  $RT$ , whence  $\frac{\Delta gw}{Tn} = RT$ .  $R$  must be here expressed in thermal units; this value has been already calculated and found equal to 2 (p. 72).

We have therefore  $\frac{\Delta gw}{Tn} = 2T$  or  $\Delta = \frac{2T^2}{w} \cdot \frac{n}{g}$ . If we compare this value with that given on p. 136 for  $\Delta$ , it follows that  $r = \frac{2T^2}{w}$ . The constant  $r$  is thus determined by the latent heat of fusion  $w$ , and the absolute temperature of fusion.

To test this theoretical result,  $r = \frac{2T^2}{w}$ , van't Hoff, to whom we owe the calculation, deduced the constants of several substances from the known values of the latent heat and the melting-points, and compared them with the empirically found constants of Raoult. The numbers are :-

	$T$	$w$	$\frac{2T^2}{w}$	$r$
Water . . . . .	273	79	1890	1850
Acetic acid . . . .	290	43.2	3880	3860
Formic acid . . . .	281.5	55.6	2840	2770
Benzene . . . . .	277.9	29.1	5300	5000
Nitro-benzene . . .	278.3	22.3	6950	7070

If we consider the comparative roughness with which some of the heats of fusion have been determined, the agreement is very satisfactory.

## CHAPTER VII

### SALT-SOLUTIONS

As has already been mentioned, a large group of substances—acids, bases, and salts, to wit—do not obey the simple laws in aqueous solution. This is no property peculiar to these substances as such, for in alcoholic and ethereal solution they behave quite normally and act as calculated from their molecular weights. In the same way water occupies no exceptional place with regard to other solvents when indifferent substances are dissolved in it. The exceptional behaviour only appears when the above substances are dissolved in water, and is a result of the mutual action of both factors.\*

The molecular weight of these substances when determined from their aqueous solutions by any of the previous methods is always smaller than it ought to be according to the chemical formula. If  $M$  is the molecular weight corresponding to the formula, and  $M_w$  that found in aqueous solution, we may put  $M = iM_w$ , where  $i$  is a number always greater than 1 and possibly as large as 4 or 5. It is to be noted that all the methods give the same value of  $i$  for one and the same solution. A solution of potassium chloride for which  $i$  is nearly equal to 2, exhibits not only twice the depression of the freezing-point that corresponds to the formula, but the lowering of vapour pressure and the osmotic pressure are too great in the same ratio of 2 : 1. The number  $i$  is therefore not dependent on the method employed, but only on the nature of the dissolved substance, and in a certain measure on the concentration and the temperature.

The explanation of these phenomena has already been indicated. We must assume that the substances in question are dissociated in their solutions, *i.e.* split up into smaller molecules, just as ammonium chloride is dissociated in the vaporous state. It is true that here the dissociation is of a peculiar kind, connected in the most intimate way

It may be well to state here what will be seen later to be of decisive importance for the theory of these phenomena—namely, that solutions which are thus exceptional, and only such, are electrolytes. The two properties are always associated, not a single exception being known.



with the electrical properties of the solutions, as will be shown more in detail in Book IX., on Electrochemistry. At this place it need only be mentioned that, proper consideration of the factor  $i$  being taken, the solutions of acids, bases, and salts also obey the general laws of solutions.

Numerous observations have been made as to the properties of salt-solutions, which have led to some more or less general relations. Valson's Law of Moduli (1874) is an example. If the specific gravities of different solutions containing equivalent quantities of salts in the same quantity of water be so arranged in a table that all salts with the same base come into one perpendicular column, and those with the same acid into one horizontal row, the difference between corresponding members of the series in both directions is constant. From this it follows that the specific gravity of equivalent salt-solutions is composed additively of two members, one of which depends only on the acid, the other only on the base.

Valson chose a normal ammonium chloride solution (49.5 g. per litre), whose specific gravity is 1.015, as his starting-point and determined the following addenda, expressed in units of the third place, for the calculation of the specific gravities of other solutions —

Potassium .	30	Iron .	37	Chlorides .	0
Sodium .	25	Zinc .	41	Bromides .	34
Calcium .	27	Copper .	42	Iodides .	64
Magnesium .	20	Cadmium .	61	Sulphates .	20
Strontium .	55	Lead .	103	Nitrates .	15
Barium .	73	Silver .	105	Carbonates .	14
Manganese .	37			Bicarbonates .	16

Thus if we want to determine the density of a normal solution of calcium nitrate, we must add to 1.015 the constant .027 for calcium and .015 for nitric acid, which gives 1.057, agreeing very nearly with experiment.

This relation has been extended by Bender (1883), who showed that the density of a solution containing  $n$  equivalents of a salt could be obtained by adding to the density of an ammonium chloride solution of  $n$  equivalents the  $n$ -fold value of the moduli. This new relation is, however, by no means perfectly exact.

The densities of the solutions of one and the same salt in water are not, as one might suppose, of such magnitude that the excess of these values over unity is proportional to the quantity of salt dissolved. This would be approximately the case if a concentrated salt solution could be mixed with water without change of volume. A contraction, however, regularly takes place; the volume of the dilute solution becomes smaller, and its specific gravity therefore greater than it ought to be according to calculation.

All these relations appear much clearer if instead of the specific

gravity we consider the specific volume. Ostwald (1878) made a series of detailed experiments on the change of volume during chemical processes, from which resulted the following general conclusions.

If an acid is neutralised by a base, both being in aqueous solution, an increase of volume takes place if the base is potash or soda, a diminution of volume if it is ammonia. The change of volume depends on the nature of the acid; it is some 20 c. cm. when 1 l. of normal potash solution is mixed with 1 l. of normal hydrochloric acid, and falls to 6.3 c. cm. with potash and isobutyric acid.

If the changes of volume given by a base with the acids  $A_1, A_2, A_3, \dots$  be compared with those given by another base with the same acids, it will be found that the differences for all the acids are the same—are consequently independent of the nature of the acids. Similarly the differences between the changes of volume given by different acids with the same base have the same value for all bases.

The change of volume on neutralisation is thus additively composed of two terms, one of which is determined only by the base, the other only by the acid; the particular nature of the salt formed having no influence on the result, provided that all remains dissolved.

The connection between this fact and Valson's Law of Moduli is obvious. The volume  $v$  of a salt-solution is given by the formula  $v = a + b + d_a + d_b$ ; it is equal to the sum of the volumes of the solutions of the acid, and of the base plus a change of volume  $d_a$  dependent on the acid alone, and one  $d_b$  dependent on the base alone. If we write the equation in the form  $v = (a + d_a) + (b + d_b)$  we see still more plainly that the volume of the salt-solution is represented as the sum of two volumes determined respectively by the base and by the acid. As now the volumes are inversely as the densities, and, as in the present case they do not differ very much from unity, we may put  $\frac{1}{1 + a + \beta} = 1 - a - \beta$  (where  $a$  and  $\beta$  are the "moduli"), and consequently perceive that the law of moduli is a consequence of the law of volumes for neutralisation.

The above relations show that the nature of the salt produced by neutralisation in aqueous solution has no specific influence, but only the nature of the two components. This circumstance likewise points to the conclusion already indicated, which will be more thoroughly established in the sequel, that in salt-solutions the two components of the salts, metal and acid radical, exist almost independent of one another.

## BOOK V

### THE PROPERTIES OF SOLIDS

#### CHAPTER I

##### GENERAL PROPERTIES

SOLIDS differ from liquids by possessing not only a proper volume but also a proper form. Together with the causes which in liquids preserve the mean distance of the particles unchanged, and thus determine the volume, we have also in the case of solid substances causes which determine the relative position of the particles—the form.

According to the molecular hypothesis a solid is consequently a body whose molecules so influence each other that their displacement relatively to each other is not easily brought about. We can explain such a state by assuming that in the interaction of the molecules their form comes into play, inasmuch as they act differently in different directions, and an expenditure of work is necessary to alter their relative positions.

The passage from liquids to solids is gradual. As its internal friction increases, a liquid assumes more and more the properties of a solid. That some bodies undoubtedly solid, such as glass for instance, still retain a trace of liquid properties is shown by the well-known fact that a long straight glass rod placed horizontally and supported only at its ends gradually “sags” and becomes bent. Its particles follow the influence of gravity like those of a liquid, only incomparably more slowly.

Besides this property of slowly suffering permanent deformation, which probably all solids possess, though in very different degree, they **have** also the capability of experiencing transitory deformations which disappear immediately the deforming cause is removed. We distinguish here two essentially different properties, one of which

corresponds to the compressibility of liquids, while the other is peculiar to solids alone and comes into play when they suffer change of form, as by bending, torsion, and the like. The latter we call elasticity. It is impossible to separate this entirely from the compressibility, as changes of volume always accompany changes of form, and the observed coefficients of elasticity (so-called) are really functions of both values.

Solid substances occur in two very different states, to which the names amorphous and crystalline have been given. Solids in the first state only can be arranged in a continuous series with liquids; they may be looked upon as liquids having very great internal friction. Quite a new condition is added in the crystalline state. The molecules are no longer arranged haphazard as in liquids and amorphous solids, but their form has in some way conditioned a regular arrangement, and this makes itself apparent in the corresponding regular form of the whole mass and in the differences exhibited by numerous properties in different directions.

To get an idea of the difference between the two states we can imagine the amorphous body as a confused heap of bricks, while the crystalline body is a regular structure made by their arrangement in layers. It should be at once mentioned that though the latter arrangement is in general the denser, it need not be so. The bricks may be built together in such a way that spaces occur between them quite regularly, so that they occupy a larger volume than when piled up without regard to any order. This explains why in certain, though rare, cases, the density of a crystalline substance is less than that of the same substance in the amorphous or even the liquid form.

## CHAPTER II

### FUSION AND SOLIDIFICATION

It has been stated above that the amorphous state forms the regular continuation of the liquid state. No sudden change takes place between them, and in particular amorphous substances have no real melting-point. This passage from one state to another is so far to be compared to that of liquids into gases under a greater than the critical pressure. The passage from the liquid to the crystalline state, on the other hand, is a sudden one; it takes place at a definite temperature, at which both states can exist together, while at other temperatures only one of the two forms is stable. This is comparable to the passage of a vapour into a liquid below the critical pressure, and indeed the similarity of the two phenomena is very far-reaching.

If a liquid capable of passing into the crystalline state is slowly and carefully cooled, no separation in general takes place when the temperature is reached at which the crystalline form can exist along with the liquid, but the liquid, by increase of its viscosity, approaches the amorphous solid state. Such liquids, when brought into contact with a small quantity of the crystalline solid, immediately pass more or less completely into the crystalline state; they become at the same time warm from the heat produced by the solidification, but naturally their temperature does not rise higher than the melting-point.

If care be taken that a little of the crystalline substance is present beforehand, then the phenomenon of overcooling does not appear, but the passage from the liquid to the crystalline state takes place quite regularly at a definite temperature, which remains constant during the whole transformation, as the heat lost by conduction and radiation is exactly replaced by the heat of solidification until the last particle has become solid.

In this respect there is a complete analogy to vapours. These also may be overcooled, but the state of overcooling ceases to exist as soon as a little of the liquid is introduced (p. 84).

To the reverse phenomenon, the superheating of liquids (p. 84), we know of no analogue in crystalline substances. If the latter are

heated they begin to liquefy or melt at a definite temperature identical with their point of solidification, and notwithstanding the external supply of heat, remain at this temperature until all is liquid, the heat being used up in the process of liquefaction.

The similarity to the passage from the liquid to the gaseous state, and *vice versa*, is still further to be observed in the dependence of the melting as well as of the boiling point on the external pressure. The latter always rises with increase of pressure (for the vapour in every case occupies a larger volume than the liquid), whereas the melting-point only does so when the substance on fusion increases in volume. If the volume diminishes, as in the case of the melting of ice, then the melting-point sinks as the pressure increases (James Thomson 1849, Bunsen 1850). The influence of pressure is, however, very small, *e.g.* 1 atm. lowers the melting-point of ice  $0.007^{\circ}$ .

The solidification of an overcooled liquid on contact with a crystal of the same substance is an effect produced exclusively by the latter. If, for instance, we dip into fused sodium thiosulphate cooled to the ordinary temperature a glass rod covered with the same salt, crystals begin at once to develop round the rod. If these are then removed carefully from the liquid so that no crystalline particle remains behind, there is no further solidification; the liquid state is retained. An overcooled liquid therefore is not *per se* in an unstable state; this is only the case when some of the solid substance is present.

We readily find an explanation of this from the molecular theory. In a liquid the molecules move about quite confusedly and assume all conceivable relative positions. No special position is favoured. A crystal of the same substance, if introduced when the temperature is above the melting-point, will liquefy, for then the kinetic energy of molecular motion is greater than the work necessary to break up the crystalline aggregate. If the temperature is just at the melting-point, the two magnitudes balance each other. As many molecules leave the crystal in a given time as are added to it, so that in general its size remains unaltered. If the temperature is lower than the point of solidification fewer molecules are freed from the crystal than are captured by it—the crystal grows.

If now the liquid is allowed to cool, no crystal being present, the molecules receive no impulse to assume a regular arrangement, and there is “overcooling.” The kinetic energy of the molecules decreases, they get nearer and nearer to each other, and it may happen that amongst the many encounters one may occur so that the molecules will just be in the specially stable regular arrangement that determines the crystalline form. The circumstances are then given under which the liquid crystallises spontaneously; the molecules add themselves gradually to the crystalline nucleus, those being retained that approach in a suitable way, until the melting-point is reached on account of the rise of temperature, and then equal numbers of molecules enter and leave the crystal.

If a crystal is introduced into the supercooled liquid before it begins to crystallise spontaneously, the process described comes into operation at once; if the crystal is again removed, there is no longer any cause for new crystals separating out.

The possibility of supercooling obviously depends, according to the above view, on the ease with which the molecules fortuitously come into the required regular position. Mobile liquids will be much more difficult to supercool than viscous liquids, and the crystallisation of a given liquid will take place more readily the larger quantity we take of it. For, since it suffices that the requisite arrangement of the molecules should occur at one spot, the probability of crystallisation evidently increases with the total number of molecules, *i.e.* with the quantity of the supercooled liquid.

## CHAPTER III

### SOLUTIONS OF SOLIDS IN LIQUIDS

THE solution of solids in liquids and their separation from solution show even greater similarity to the processes of vaporisation and condensation than do the melting and solidification of solids. If a crystalline solid is brought into contact with a suitable liquid, its particles become distributed through the liquid—it dissolves. This process of solution proceeds until there has been reached in the liquid a definite concentration dependent on the nature of both substances and on the temperature; there is then equilibrium. The similarity to vaporisation is complete when we remember that dissolved substances too have a pressure—the osmotic pressure (p. 127); solution, like vaporisation, continues until the proper pressure is established.

The equilibrium between the solution and the solid has its origin in their mutual action, and is therefore dependent on the nature of both. A definite solution pressure may be ascribed to every solid with respect to any given liquid at a given temperature, just as each liquid possesses a definite vapour pressure. Solution, like vaporisation, will go on until the opposing pressure has become equal to the solution pressure (Nernst, 1889).

Consequently the solubility of a chemical compound is only determined when it is stated what definite solid is referred to. Calcium sulphate is much more soluble in water when anhydrous than in the form of hydrated crystalline gypsum. We cannot, therefore, speak at all of the solubility of calcium sulphate unless we specify whether the anhydrous or the hydrated salt is meant.

For reasons both practical and theoretical much work has been done on the solubility of solids, especially of salts in water. The relation between temperature and solubility is most clearly shown by curves, the temperatures being the abscissæ and the quantities dissolved by 100 parts of the solvent the ordinates. (Figs. 19-22.) We see that most of the curves are of such a form that they rise towards the right at an increasing rate, thus resembling the curves of vapour pressure. There are, however, substances which show decreasing solubility with rise of temperature, *e.g.* calcium hydroxide,



calcium isobutyrate. A close connection exists between the influence of temperature on the solubility and the change of temperature on solution. Substances whose almost saturated solutions would cool on taking up a further quantity of the solid increase in solubility with the temperature, and

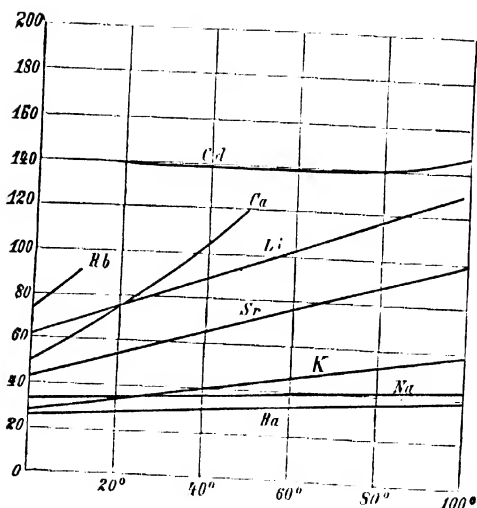


FIG. 19.—Chlorides.

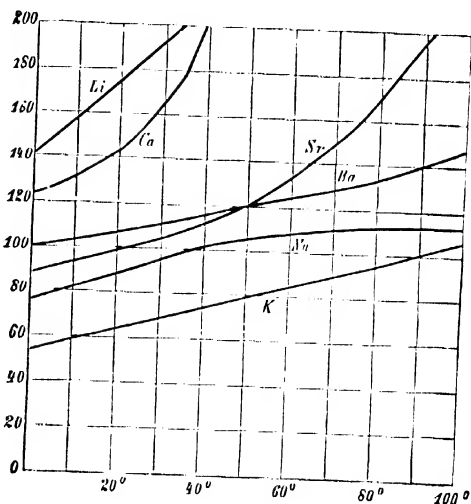


FIG. 20.—Bromides.

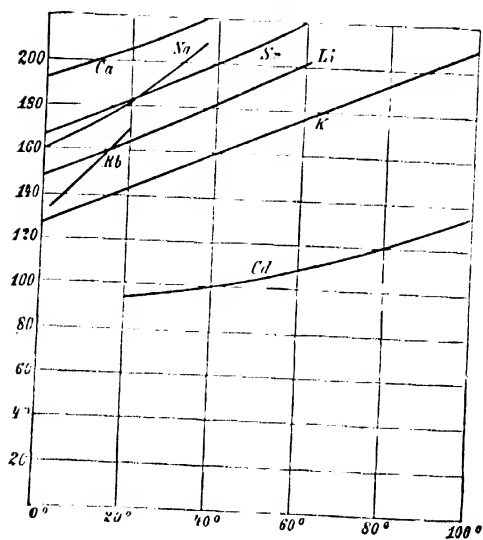


FIG. 21.—Iodides.

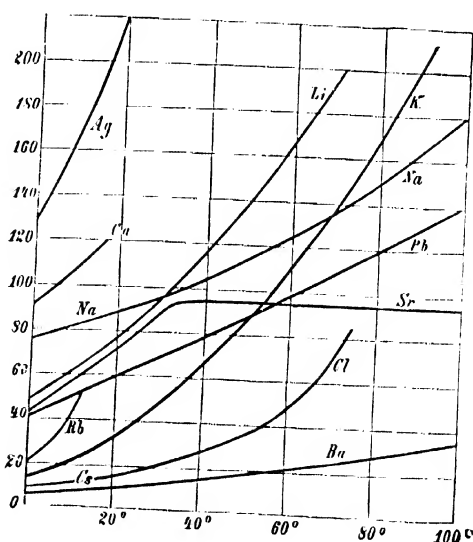


FIG. 22.—Nitrates.

*vice versa*. This is a special case of a perfectly general principle, viz. when a system is in equilibrium and any one of the conditions of equilibrium is forcibly altered, the accompanying phenomena take place in such a way as to resist the compulsive force.

Some of the curves are evidently made up of several distinct portions, e.g. strontium nitrate, Fig. 22. In such cases the separate portions belong to different solids, usually hydrates with different quantities of water.

Want of attention to the circumstance that solubility can only be defined with reference to a perfectly definite solid has led to much misconception. If Glauber's salt,  $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$ , is dissolved in water the solvent with increasing temperature takes up more and more of the salt until  $33^\circ$  is reached. If now the mixture of the salt and water is further heated, the solubility decreases until at  $100^\circ$  it is only half as great as at  $33^\circ$ . The usual explanation is that the hydrated salt is contained in the solution below  $33^\circ$ , and the anhydrous salt above  $33^\circ$ . This, however, is wrong, for the solutions of sodium sulphate show no discontinuity in any property at this point.

The explanation should rather be that  $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$  only exists below  $33^\circ$ ; if it is heated alone above this temperature the crystals melt and anhydrous salt separates. The break in the curve therefore is not due to the existence of different salts in the solution, but to the presence of different salts in contact with the solution. The solubility up to  $33^\circ$  is that of Glauber's salt, above  $33^\circ$  it is that of the anhydrous sulphate; at  $33^\circ$  the two curves meet. The curve of the anhydrous salt may be traced below  $33^\circ$  by introducing this salt into the solution. Much more is dissolved than corresponds to the solubility of the hydrated salt.

The phenomena in supersaturated solutions are now comprehensible. If a salt solution is allowed to cool or to evaporate there is in general no reason for the deposition of a solid. If, however, the osmotic pressure in the solution exceeds the solution pressure of one of the salts which may separate, and a particle of this salt is brought into contact with the solution, a rapid separation of the salt results and continues until a state of equilibrium is reached. Such solutions are called supersaturated, but it is clear that the supersaturation is only with respect to a definite solid; without this reference the expression is meaningless.

From a cold solution of sodium sulphate there can separate  $\text{Na}_2\text{SO}_4 + 7\text{H}_2\text{O}$  as well as  $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$ . As the former is more soluble than the latter, solutions can be prepared which crystallise at once on contact with  $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$ , *i.e.* are supersaturated with respect to this salt, while on the other hand they can still dissolve small quantities of  $\text{Na}_2\text{SO}_4 + 7\text{H}_2\text{O}$ , *i.e.* are not yet saturated with respect to this substance. If such solutions are further cooled they may be supersaturated with reference to both salts. The relative character of the two phenomena is here specially manifest.

The molecular hypothesis accounts for these processes in the same way as it did for fusion and solidification, so that the considerations on p. 147 may be applied here almost without alteration. On contact of a soluble substance with its solvent its molecules are offered the opportunity of unconstrained movement; they enter the solvent until in the same time equal numbers of molecules leave the solid and are again taken up by it. This evidently depends on the number of molecules contained in unit volume of the solution, *i.e.* on the concentration. If

the solid is brought into a solution of greater concentration it will take up more molecules than it gives out; the liquid is "supersaturated" and the crystal grows. If the crystal is removed, the cause of the separation is no more at work and the solution remains "supersaturated." The spontaneous crystallisation of a supersaturated solution depends on exactly the same circumstances as the solidification of an overcooled fused mass, to which the student may again refer (p. 147).

It should be stated in conclusion that the application of these relations is by no means limited to aqueous solutions; they hold for solutions with other solvents as well as for fusions of all kinds. In particular they play a decisive part—one hitherto far too much neglected—in the crystallisation of melted silicates, as in the case of lavas and other eruptive rocks, and form the foundation for the right comprehension of these exceedingly important geological phenomena.

The above conception of the saturation of solutions puts us at once in a position to understand a class of phenomena which formerly presented great difficulties, viz. the solubility of mixtures of salts. On this subject we have researches by Kopp (1840), Karsten (1841), Hauer (1860), and in particular by Rüdorff (1873), the chief results of which are the following.

Certain salts when together in contact with water dissolve in such a way that a solution of definite concentration is formed at a given temperature, its nature being independent of the quantity of the salts present, provided only that they are in excess. Such salts are the chlorides and nitrates of the alkali metals and of ammonia, potassium and lead nitrates, the chlorides of barium and ammonium, the sulphates of sodium and copper, and the chlorides of sodium and copper.

Other salts have the property that they displace each other from solution, so that quite different saturated solutions are obtained according to the different proportions of salts taken. These salts fall into two groups; they are either isomorphous, or they can form double salts. The two groups behave, however, differently, a fact hitherto unnoticed. If one of the components of a double salt is dissolved in a solution of the latter by warming and the whole then allowed to crystallise, it is found that the quantity of the other component in the resulting solution is diminished. If the process be repeated a solution of constant composition is finally obtained, from which the last portion of the salt cannot be displaced. The same thing happens on addition of the other component. Instead of the pure solutions yielded by the groups of salts of the first type, we obtain two limiting solutions of constant composition, together with all intermediate ratios.

Isomorphous salts displace each other, in general, completely if the solution is repeatedly treated in the hot state with one of the pair and allowed to crystallise.

The explanation of this behaviour is simple. As the nature of the solution is determined by that of the solid body in contact with it, a solution of constant composition will always be obtained when the composition of the solid is constant. This is the case with salts that do not crystallise together, neither as double salts nor as isomorphous mixtures. From solutions of a mixture of them saturated in the hot state the salts separate out unchanged, and the solution is saturated with respect to both salts, however much of each may be present. The phenomenon is perfectly analogous to that of the vaporisation of immiscible liquids, the vapour in this case having a composition independent of the proportions of the liquids present.

When a double salt is dissolved, a solution saturated with reference to it is obtained. If now an excess of one component is added, an additional factor is introduced—the solubility of the simple salt. With sufficient quantities of the latter a solution must at last be formed which is saturated both for the double and for the simple salt, and there is in general a much smaller quantity of the double salt dissolved than is contained in the saturated solution of it alone. The same considerations are applicable to the other component; here also we must get a solution simultaneously saturated for the double and the simple salt. On the whole, then, there are three saturated solutions: one for the double salt alone, and one each for it and one of the two simple salts. Between the two last solutions all possible gradations can be obtained; these, however, are not stable in contact with the solids, but are always undergoing a slow transformation.

For substances which can form isomorphous mixtures in all proportions there is a different state of saturation for each composition of the solid. Equilibrium is established with respect to a solid (the deposited isomorphous mixture) which can have any composition between those of the two pure salts, so that there is here no question of a definite solubility at all.

## CHAPTER IV

### CRYSTALS

It has already been several times stated that solids are often so built up that their particles are arranged according to some definite law. This regular arrangement is seen wherever direction comes into question, for example in external form, elasticity, optical properties, thermal conductivity, and the like. While these properties have equal values in all directions in amorphous bodies, they are only equal in parallel directions in crystals, as we call such bodies with regular structure; in other directions they are in general different.

Of the properties here in question the external form was the first to be noticed and investigated. Nicolas Steno (1669) discovered the law that while in different crystals of the same substance the form and size of the faces may alter in any way, the angles between the faces remain always the same.

Another regularity among the different faces of a crystal was found by Haüy (1781), who stated it as follows:—If we imagine, and this is always possible, that the simplest forms of a crystal are built up of prismatic elements with definite angles and proportions of the edges, then we can with similar prismatic elements construct all other forms occurring on the crystal so that the surfaces drawn through the corresponding corners of the elementary prisms represent the faces of the crystal.

Crystallography received its present form from Weiss (1809), who introduced the idea of referring the different crystalline forms to definite systems of axes. The following laws on this method of representation correspond to the two just mentioned. Firstly, every substance has a system of axes whose angles and relative lengths have definite values; and, secondly, the different faces occurring on the crystal, when moved parallel to themselves to cut one axis in a given point, cut the other axes so that the segments of any of these stand in simple rational proportions to each other.

To these two laws must be added a third,—the law of symmetry, the recognition of which is also partially due to Haüy. It was

first established completely only very much later, by von Lang (1865). It is to the effect that crystals are in general symmetrical structures, *i.e.* that planes may be drawn through them with respect to which the parts of the crystal on either side are to each other as object and reflected image. The number and position of these planes are different, and a systematic classification of crystals can be made by means of them.

Corresponding to their increasing symmetry, crystals are divided into six groups, which will now be shortly discussed, so far as a knowledge of them is necessary for our general theoretical purposes.

The simplest and least regular system is the asymmetric. The system of axes to which it may be referred consists of three unequal straight lines all inclined to each other. There is no plane of symmetry, the regularity of formation being confined to the fact that in a fully developed crystal each face has a parallel face opposite it. If the possible eight planes are laid through the ends of the axes we obtain the fundamental form of the system, in which the opposite pairs of faces only are equivalent. As independent forms of the asymmetric system we have, therefore, only parallel pairs of surfaces.

In the monosymmetric system there is one plane of symmetry. The system of axes consists of two inclined straight lines, and a third perpendicular to the plane of the first two—the plane of symmetry. If any plane is made to pass through the axes, this conditions a symmetrically situated second plane lying as the mirror image of the first reflected in the plane of symmetry. To each of these two planes we have the opposed parallel planes, so that the forms of the monosymmetric system are composed of open four-faced or prismatic figures. Each of these can pass into a pair of parallel faces by two opposite angles becoming more and more acute. The forms of the monosymmetric system are therefore composed of open prisms and parallel pairs of surfaces. The octahedral fundamental form, obtained by laying eight planes through the ends of the axes, is merely a combination of two independent prisms.

In the rhombic system there are three planes of symmetry, and the axes are three unequal straight lines all intersecting at right angles. If any plane be made to cut all the axes, the first plane of symmetry determines a second symmetrically situated plane. The second plane of symmetry doubles this number, and thus we have four planes. The third plane of symmetry (determined by the presence of the other two) generates no new planes, but only the opposed parallel faces, so that there is produced an eight-faced closed form (the rhombic pyramid of Fig. 23). By choosing this as the fundamental form we can get the derived pyramids by rational multiplication or division of one or two axes (Figs. 24 and 25) according to the fundamental law of crystallography.

If one of the axes increases indefinitely the pyramid passes finally

into a prism, there being three sorts of these prisms, one parallel to each axis. If two axes are prolonged to infinity we get parallel pairs of surfaces, there being again three distinct pairs, one at right angles to each of the three axes. All the forms of the rhombic system are composed of these three fundamental types

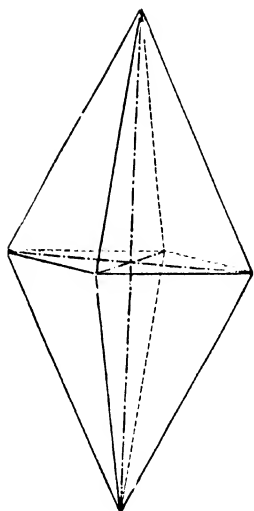


FIG. 23.

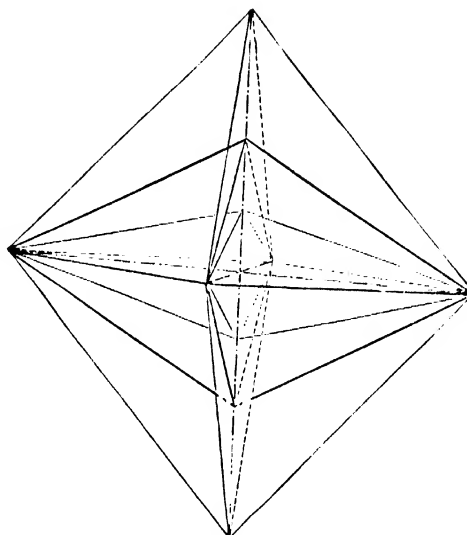


FIG. 24.

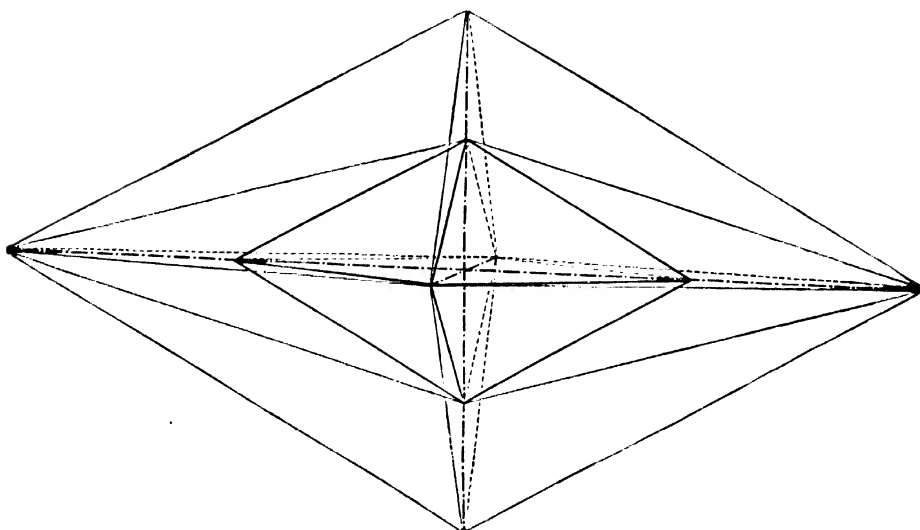


FIG. 25.

If two of the planes of symmetry of the rhombic system become equivalent we obtain the quadratic system. Corresponding to the condition above mentioned, the axes lying in the equivalent planes are also equivalent, so that the system of axes consists of three straight lines at right angles to each other, two being equal but

different from the third. If the right angle between the two equal axes is bisected, and a plane be made to contain the bisecting line and the third axis, the two first axes are symmetrical with respect to this plane, which, together with a perpendicular plane (also passing through the third axis), is therefore to be conceived as a plane of symmetry. The rhombic system has consequently five planes of symmetry.

If any face cut the three axes, it will be doubled by the first plane of symmetry; the second will determine four, and the third eight similar faces. The fourth and fifth planes of symmetry generate only parallel faces. The general form is thus composed of sixteen planes giving an eight-sided double pyramid (Fig. 26). It is called the biquadratic pyramid, and may assume different forms by alteration in rational proportions of the singular or principal axis, as well as of the equal or secondary axes.

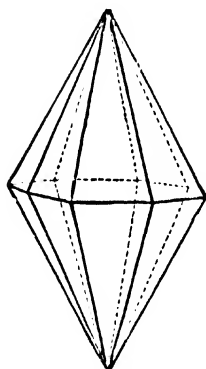


FIG. 26.

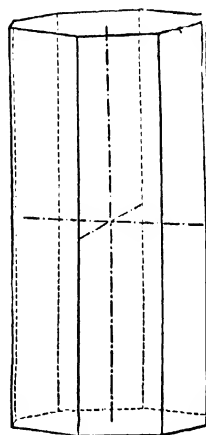


FIG. 27.

If the principal axis be cut at an ever-increasing distance, biquadratic prisms (Fig. 27) are finally obtained. When the two secondary axes are cut at equal distances from their intersection the neighbouring faces coincide in pairs, so that we obtain an eight-sided figure—the quadratic pyramid. An exactly similar form is produced when any one of the secondary axes is indefinitely extended. Both forms, by prolongation of the principal axis, pass into four-sided prisms. By simultaneous extension of both secondary axes a two-sided figure is got, the faces being at right angles to the principal axis.

The hexagonal system, in many respects similar to the quadratic, is obtained when not four planes of symmetry at  $45^\circ$ , but three at  $60^\circ$  contain the principal axis. We thus get a system of axes consisting of three equal straight lines in one plane intersecting at an angle of  $60^\circ$ , and a fourth line perpendicular to the plane of the others.



The most general form is a twelve-sided double pyramid (Fig. 28), which passes by gradual simplification into the hexagonal pyramid (Fig. 29), the dihexagonal prism (Fig. 30), the hexagonal prism (Fig. 31), which can be obtained in two positions, and lastly into a pair of faces at right angles to the principal axis. The derivation of the forms is quite the same as in the quadratic system.

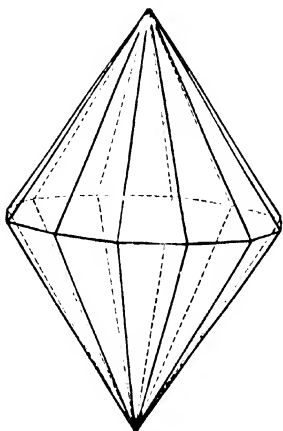


FIG. 28.

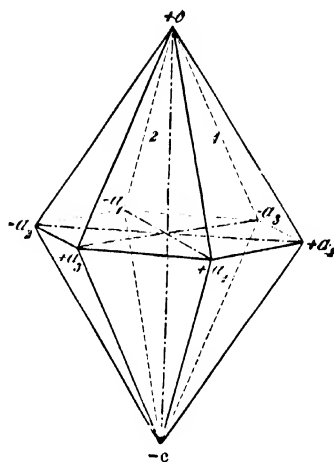


FIG. 29.

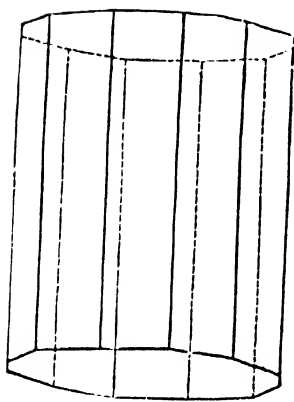


FIG. 30.

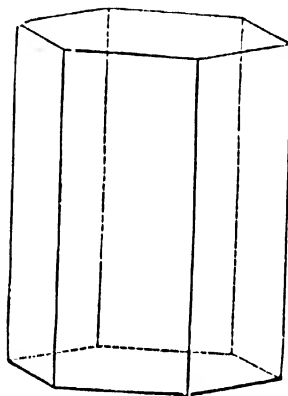


FIG. 31.

The regular system results when all the planes of symmetry of the quadratic system are made equivalent. The axes are then three equal straight lines at right angles, and in addition to the three principal planes of symmetry there are six others. The group of sixteen faces developed as the most general form of the quadratic system is repeated at each of the three axes, so that here the most general form is a forty-eight-sided figure (Fig. 32). By gradual simplification this hexakisoctahedron passes into all the other forms of the regular system. If one axis is taken as the unit and the others made equal

to the same multiple of it, the icositetrahedron (Fig. 33) is the result ; if two axes are made equal to unity, the pyramid octahedron (Fig. 34) is produced. When all the axes are equal we have the fundamental form, the octahedron (Fig. 35). One axis becoming infinite gives from

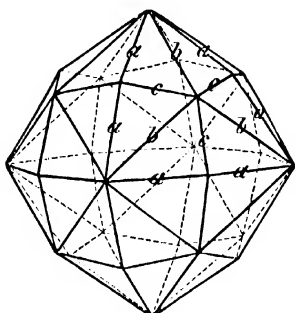


FIG. 32.

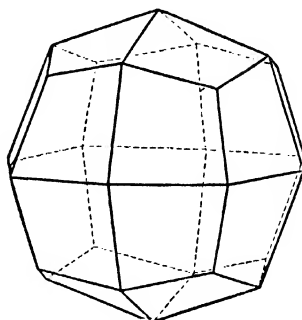


FIG. 33.

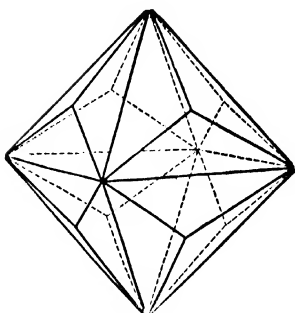


FIG. 34.

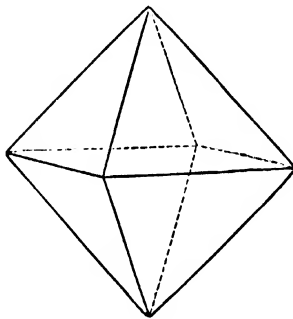


FIG. 35.

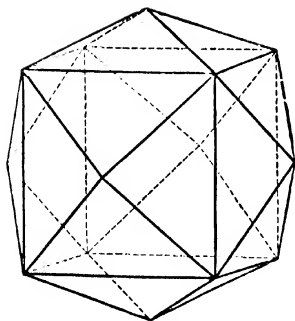


FIG. 36.

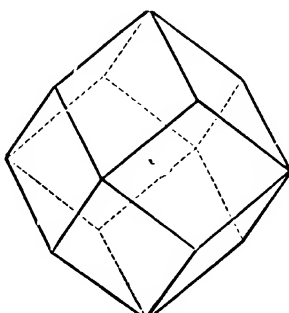


FIG. 37.

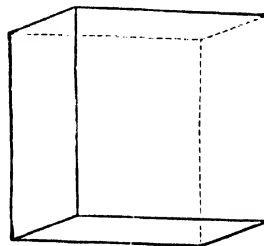


FIG. 38.

the hexakisoctahedron the pyramid cube (Fig. 36) ; if, in addition, the two other axes are equal, the rhombic dodecahedron (Fig. 37) results ; finally, if two axes are cut by the faces only at infinity, we get the cube (Fig. 38).

Besides these forms, which are generated by the complete development of all faces demanded by the relations of symmetry, there are others derived

from the first kind by the regular omission of certain faces. Such hemihedral forms are most numerous in the most symmetrical, the regular system; they also, however, occur in the quadratic and hexagonal systems. We may be spared from entering into this subject in detail, as its treatment is to be found in any text-book of crystallography.

It has been already emphasised that the regular crystalline forms discussed above are only the outward sign of the regularity of the internal arrangement of the particles throughout the whole substance. The question therefore arises whether it is not possible to arrive at such a conception of this regularity that the crystalline form, as well as the other relations to be discussed hereafter, must of necessity follow. Such ideas have been developed by Frankenheim (1832-56), Bravais (1849), Möbius (1849), and Sohncke (since 1867), and have led to the desired result.

Let us imagine a system of points in space, fulfilling the condition that the arrangement round any one point is the same as round any other. If we join any of these points with a neighbouring one, the straight line formed will, when produced in both directions, pass through points distant from the original points by the length of the original line; for by our assumption a third point must lie in the same relative position to the second as the second does to the first: the straight line will thus join up an infinite range of equidistant points. If we now draw a line from the point first considered to another neighbouring point the same thing holds, and it is also true for every parallel to the first straight line drawn through a point of the second, and *vice versa*. The two systems of parallels obtained by this construction lie in the same plane, and their intersections contain all the points of the system which are in that plane. The arrangement characteristic of crystals thus leads us in the first instance to two systems of co-planar equidistant parallels intersecting at a definite angle. If we add the limitation that the two determining straight lines be drawn from the point of origin to the two nearest points, it can be proved that the angle must lie between  $60^\circ$  and  $90^\circ$ .

If we now draw a third straight line to a neighbouring point not lying in the same plane as the others, what we found above applies also to this line and to all parallel lines drawn through the points in the plane. All possible points arranged according to our assumption are thus determined as the intersections of three systems of parallel equidistant planes, the angles between which are subject to the condition already stated for the angle between the parallel lines. If no further condition is added we have the case of least symmetry, the asymmetric system.

But now, if we add the restriction that there shall be one plane of symmetry, this plane must evidently be at right angles to one of the planes determined by two ranges of points, and bisect the angle between these ranges; otherwise the condition of symmetry, that the arrangement on one side of the plane should be the mirror image of the arrangement on the other, cannot be fulfilled. Again, the distances between neighbouring lines in the two systems of parallels contained by the plane of the ranges must

be equal. For, if we imagine one system to be drawn till it cuts the plane of symmetry, its mirror image must appear on the other side. If now the two systems of parallels be infinitely produced, the net in the plane is fully specified. We come, therefore, to the conclusion that a plane of symmetry at right angles to another plane determines in the latter a network of points with a rhombic mesh, through a diagonal of which it passes. As regards the points without the plane, we must first of all recollect that every plane containing them, and parallel to that just considered, must have exactly the same arrangement of points as the latter. Such a second field of points may thus be obtained by moving the first parallel to itself. But the demands of the law of symmetry must be satisfied. In general a parallel movement would result in the number of points being doubled by reflection in the plane of symmetry, but this must not be the case—the points and their images must coincide; the field must therefore be shifted so that each point moves along a line parallel to the plane of symmetry. The projections on the original field of the points external to it must consequently fall on the diagonal of the rhombs through which the planes of symmetry pass. As fundamental form of this three-dimensional system of points or “space net” we thus obtain a parallelepiped with a rhombic base, each pair of intersecting sides being equally inclined to the base. By drawing the diagonals of the base, and then joining their point of intersection with the corresponding point of the opposite face we get a system of three axes, two of which are at right angles to each other and the third inclined to both. This, as we have seen, is characteristic of the monosymmetric system.

Symmetry in the plane may be attained in another way, namely, by arranging one series of parallel ranges at right angles to the plane of symmetry and the other parallel to it, the distance between adjacent ranges in the second series being different from that in the first. The proof that this arrangement is in no way essentially different from the above would lead us too far, and so will be omitted.

We will now assume that there exists a second plane of symmetry. This necessarily calls into existence a third, which is its mirror image in the first; again, the mirror image of the first in the second determines a fourth; each of these new planes of symmetry determines three others, and so it goes on. Two planes of symmetry placed thus at random give rise to an infinite number of new planes, all containing the same straight line. This, however, on our original assumption is impossible, so we must look for special positions in which the number of planes of symmetry remains finite. The condition for this is that the angle be  $\frac{180^\circ}{n}$ , where  $n$  is a whole number.

We shall first take  $n=2$ ; the two planes cut at right angles. For the reasons given above they must both be perpendicular to a field of points. The ranges of this field must be symmetrical with respect to both planes, which condition is fulfilled either by the points forming rhombs that have the planes of symmetry for their two diagonals, or by the ranges being at right angles to each other and parallel to the planes of symmetry. The mesh of the net formed by the field of points is thus either rhombic or rectangular. The points of the parallel nets can likewise assume two

positions; they may lie simultaneously in both planes of symmetry, *i.e.* perpendicularly over the lower points, or they may lie over the points of intersection of the diagonals. In both cases this takes place above and below the plane considered, which consequently proves also to be a plane of symmetry. The demonstration holds in the same way for every system of more than two planes of symmetry passing through the same straight line, so that we can state in general that two or more planes of symmetry meeting in a straight line determine another such plane at right angles to that line.

Let us now reconsider our nets. When the points in the parallel plane are vertically above the middle points of the diagonals, the points of the third plane lie above those of the first. We can therefore consider such a system as a combination of two interpenetrating space nets. In all cases we arrive at three mutually perpendicular axes, which are not equivalent; this is the characteristic of the rhombic system.

The second plane of symmetry may now be determined by making  $n = 3$ , the angle being in this case  $60^\circ$ . To the first and second there is at once added a third, also at an angle of  $60^\circ$ . These are all perpendicular to the original field of points and equivalent to one another. The only possible distribution of points in the field is that into three systems of ranges each parallel to a plane of symmetry; the points form rhombs of  $60^\circ$  and  $120^\circ$ . The first parallel plane can either have its points vertically over the original points or over the centres of the rhombs; in the latter case the points of the second parallel plane are situated vertically above the original points. For the same reasons as before the original field is also a plane of symmetry, so that the whole system has four in all, three making with each other angles of  $60^\circ$  and containing the same straight line, and one perpendicular to this line. The axes are determined by the lines of intersection of the four planes of symmetry, so that we have the hexagonal system with three equivalent axes at  $60^\circ$  in one plane, and a fourth at right angles to these.

For  $n = 4$  there appears a second plane of symmetry inclined at  $45^\circ$  to the first. These two determine other two at right angles to them; so that we have four co-axial planes, those at right angles to each other being equivalent but different from the other pair. The arrangement of points in the field can only be quadratic, and the field itself, perpendicular to the co-axial planes, must also be a plane of symmetry. The position of the points in the parallel planes is determined by the same considerations as before. The system has five axes, of which four lie in one plane and are equivalent in pairs alternately, while the fifth is at right angles to these. As a rule we only take account of one equivalent rectangular pair of the first four, considering the other pair as secondary. This is called the quadratic system.

If we put  $n = 5$  or more, we find that such a number of planes of symmetry cannot be actually realised. It was seen above that the angle contained by the lines joining a point with the two nearest points cannot be less than  $60^\circ$ , while five or more planes of symmetry would entail this. We have therefore only one step to take in order to attain the highest degree of regularity; we must make the fifth plane of symmetry of the quadratic system equivalent to two others. We then have three equivalent principal planes of symmetry all at right angles to each other, and six secondary

planes in addition. Of the corresponding nine axes we usually consider only the three equivalent and rectangular principal axes. We have thus the regular system.

The above six systems may further be grouped into three classes according to the number of their principal axes. We denote by this name those axes round which we have to turn the crystal less than  $180^\circ$  in order to bring it into congruence with itself. In the asymmetric, monosymmetric, and rhombic systems there are no principal axes; these form the first class. The hexagonal and the quadratic systems form the second class, with one principal axis. The last class, with three principal axes, contains only the regular system.

Sohncke, as already stated, has recently substituted for the above mode of consideration another in which the limitation, here tacitly assumed, that all the crystalline elements lie parallel to each other, has been dropped, and replaced by the more general assumption that round each element the others are placed in corresponding positions. They need not be parallel, but may for example be alternately parallel and at right angles. The recognition that the former exposition was subject to this limitation is credited by Sohncke to Chr. Wiener.

The result of the generalised inquiry was obtained by the use and further development of a kinematical investigation carried out by C. Jordan. It was found that in addition to the space nets discussed above there existed numerous other regular arrangements of points, which stood to the former in this relation—that they could be constructed by placing several congruent space nets within each other. Among the forms so obtained are some that offer a simple explanation of the relations of hemihedry, and even the rotation of the plane of polarisation in crystals (*vide infra*). The number of regular arrangements of points is stated to be no less than sixty-six. I cannot, however, here dwell on these interesting relations; but it may be emphasised that the theory in its application to special cases, to the crystalline habit of definite substances, seems to be of extraordinary promise.

## CHAPTER V

### ISOMORPHISM AND POLYMORPHISM

At the beginning of this century Haüy advanced as axioms the two principles that each substance had only one definite crystalline form, and that different substances necessarily possessed different forms (except in the regular system, where such are impossible). Both these principles were, however, soon found to be contradicted by experience. Klaproth (1798) had found that calc-spar and arragonite with the same composition have different forms, and this observation was confirmed by later investigations. On the other hand, substances with exactly the same form, such as the alums, the red silver ores, and the mixed vitriols, had quite different compositions. The assumption made to explain this, that the crystals merely contained the foreign substances as admixtures, was disproved by their perfect uniformity and transparency in many cases.

The matter was cleared up by Mitscherlich (1820), who in the course of his researches on the phosphates and arseniates found that these had the same crystalline form when they were of similar composition, *i.e.* when the components were alike except that one salt contained phosphorus where the other contained arsenic. A similar relation was soon found for many other compounds, so that it could be said in general, that the same crystalline form was possessed not only by identical but also by chemically similar substances.

In one case, however, *viz.* the salts  $\text{NaH}_2\text{PO}_4 + \text{H}_2\text{O}$  and  $\text{NaH}_2\text{AsO}_4 + \text{H}_2\text{O}$ , no agreement of form could be shown; but occasionally the phosphate was obtained in crystals different from the ordinary form and similar to those of the arseniate.

This was another proof that one substance can assume different forms, and Mitscherlich stated that this was possible in every case.

The phenomenon that chemically similar substances crystallise in the same form received the name of isomorphism from Mitscherlich. At first only the similarly constituted substances were called isomorphous, *e.g.* the salts  $\text{Na}_2\text{HPO}_4 + 12\text{H}_2\text{O}$  and  $\text{Na}_2\text{HAsO}_4 + 12\text{H}_2\text{O}$ . As, however, very many analogous compounds of phosphorus and arsenic are

isomorphous, it has become customary to call these elements themselves isomorphous, so that the name is applied not only to those substances having the same crystalline form, but to those elements or groups which can form similarly crystallising compounds with the same residues.

The agreement of the angles of isomorphous substances is (except in the regular system) not at all perfect; strictly speaking, homœomorphism ought to be substituted for isomorphism. The differences are sometimes greater, sometimes less, but can amount to several degrees.

A more certain criterion of the existence of isomorphism than agreement between the angles is furnished by the ability of isomorphous substances to form mixed crystals. In such crystals the isomorphous equivalent components are not in combining but in perfectly indefinite proportions, dependent entirely on the conditions of formation of the crystals. But the sum of the isomorphous elements is exactly equivalent to the quantity corresponding to the formula of either of the simple compounds; or in other words, the isomorphous elements replace each other in the ratio of their equivalents.

The properties of such mixed crystals are in general such as would be calculated from the formula of simple mixing. This has been proved for the coefficient of refraction and the specific gravity. In other cases, such as the size of the angles, there occur abnormalities still awaiting an explanation.

Isomorphism has been the cause of numerous theoretical speculations as to the form of the smallest particles, etc., but these have as yet led to no important results. On the other hand, however, the principle of isomorphism has been found exceedingly useful in the discovery and proof of chemical analogies, as will be seen later. At this place we may give a list of mutually replaceable isomorphous elements to serve as a basis for discussing such analogies—

- I. Cl, Br, I, F; Mn (in permanganates).
- II. S, Se; Te (in tellurides); Cr, Mn, Te in the acids  $H_2RO_4$ ; As and Sb in the glances  $MR_2$ .
- III. As, Sb, Bi; Te (as element); P, V (in salts); N, P (in organic bases).
- IV. K, Na, Cs, Rb, Li; Tl, Ag.
- V. Ca, Ba, Sr, Pb; Fe, Zn, Mn, Mg; Ni, Co, Cu; Ce, La, Di, Er, Y with Ca; Cu, Hg with Pb; Cd, Be, In with Zn; Tl with Pb.
- VI. Al, Fe, Cr, Mn; Ce, U in the sesquioxides.
- VII. Cu, Ag in the compounds of the lower oxides; Au.
- VIII. Pt, Ir, Pd, Rh, Ru, Os; Au, Fe, Ni; Sn, Te.
- IX. C, Si, Ti, Zr, Th, Sn; Fe, Ti.
- X. Ta, Nb.
- XI. Mo, W, Cr.



There is only a partial isomorphism between the elements separated by a semicolon.

In connection with isomorphism we have relations of morphotropy, first taken into account by Groth (1870). There are known, especially in organic chemistry, numerous substances which can be derived from each other by the replacement of one or more hydrogen atoms by other elements or radicals. Relations in the crystalline form of such compounds were often suspected. Groth showed that these relations were frequently of such a character that the proportions between the lengths of the axes only altered in one direction. For example, benzene, its oxy-derivatives, and nitro-derivatives are all rhombic; the ratio of two axes remains tolerably constant in these compounds, while the third exhibits great variations. Similar relations have been shown to exist in several other groups. A substitution often causes a change into another system, *e.g.* from the rhombic into the monosymmetric. Even then, however, there frequently remains a general agreement in the shape of the crystals and approximate equality of the analogous angles.

The clear comprehension of these relations is often rendered difficult by the above-mentioned ability of many substances to appear in different crystalline forms. To this phenomenon the name of polymorphism has been given. It is much more common than was at first suspected; in particular the crystallographic investigation of organic bodies, especially under the microscope, has shown that almost every substance can be obtained in two or more different forms when the conditions of experiment are suitably chosen.

An application of this fact may be first made to the conclusion that between the elementary composition of substances and their crystalline form there is not that connection frequently supposed to exist, according to which the latter is directly determined by the former. It rather leads us to the view that if the formal properties of molecules as they exist in gases and liquids determine the crystalline form, this can only be by the different space nets being more or less easily capable of passing through them. Besides, it is questionable if the crystalline molecules which occupy the points of the space nets do not consist of a more or less considerable number of simple molecules. In fact, we may ask still further if the conception of molecules is applicable to this case at all.

The conditions under which polymorphous forms arise are still for the most part unknown. We can distinguish between two sorts of such substances, the two classes being very different in their behaviour. An example of the first kind is offered by sulphur. This substance crystallises at ordinary temperatures in the rhombic, at higher temperatures in the monosymmetric system. All monosymmetric sulphur kept at comparatively low temperatures passes into rhombic sulphur; all rhombic sulphur heated to high temperatures changes into the

monosymmetric modification. The temperature of transformation which marks off the limits of stability of the different forms, lies, according to the measurements of Reicher, at  $95.6^{\circ}$ .

Other substances behave similarly to sulphur, *e.g.* ammonium nitrate, which crystallises in four forms with temperatures of transformation at  $35^{\circ}$ ,  $85^{\circ}$ , and  $123^{\circ}$ . Mercuric iodide, which is ordinarily red, changes when heated into a sulphur-yellow modification, which when cooled again passes into the red form.

For these substances, therefore, there is within the range of temperature at which they are solid a definite point (or several) which divides it into two (or more) parts; in one part the one form only is stable, in the other part only the other.

Benzophenone was the first clearly observed example of the second kind of polymorphic substances (Zincke, 1871). It usually crystallises in rhombic forms, which melt at  $48^{\circ}$ ; occasionally, however, in rhombohedra, melting at  $26^{\circ}$ . These rhombohedra are unstable at all temperatures up to their melting-point, for they change, mostly spontaneously, and always on contact with a rhombic crystal, into the rhombic modification. They are generally got, but not with certainty, by rapidly cooling fused benzophenone heated to a high temperature.

Similar examples of substances with a stable and an unstable form are very numerous, the unstable form being mostly obtained by rapid cooling of the melted substance. Its melting-point is always lower than that of the stable form.

The difference between the two groups lies in the relation of the temperature of transformation to the melting-points of the two forms. If the former is lower than either of the latter, there is a range of temperature between the point of transformation and the lower melting-point, within which the form unstable below the temperature of transformation is stable; this gives us the first class. If, on the other hand, the temperature of transformation is higher than the lower melting-point, there is no such range in which the second form can be stable, and we have the second class.

It is here to be observed that the instability is only to be understood with respect to transformability into the other modification. If the transformation is rendered impossible in any way (through pressure, for example), there is no instability whatever.

The rate at which the unstable changes into the stable form is extremely variable. Proceeding downwards from the temperature of transformation, it at first increases in the case of sulphur, then diminishes, to become very small at temperatures below  $0^{\circ}$ . The decreasing mobility of the separate particles at low temperatures counteracts the increasing tendency to trans-

formation, and finally effects a complete stagnation. Arragonite, for instance, is very probably a more unstable form of calcium carbonate than calc-spar at ordinary temperatures ; the change of the former into the latter, however, only takes place at a somewhat high temperature and then suddenly, while at the ordinary temperature arragonite shows not the least tendency to change.

## CHAPTER VI

### VOLUME RELATIONS OF SOLIDS

THE few indications of regular relations hitherto discovered between the volumes of solids are quite of the same nature as those which we encountered in the case of liquids. Although the difficulty of fixing a temperature of comparison is almost absent, the expansion being so small, yet a new difficulty presents itself in the fact that many solids appear in several crystalline forms, differing always in their specific and molecular volumes. We are therefore in such cases in a position to institute a proper comparison only when the substances to be compared are isomorphous; if they are not so it is impossible to judge *à priori* which of the different forms should be taken.

To this theoretical difficulty there is added a practical one. The determination of the specific gravity of solids is in itself no very difficult operation, the methods with the pyknometer and the hydrostatic balance easily admitting of measurements accurate to a tenth of a per-cent. It is, however, excessively difficult to get the substances, mostly crystals, in a state permitting exact determinations to be made. When substances crystallise from solution, the crystals formed very frequently enclose bubbles of the mother liquor, which lessen the specific gravity proportionately more the larger it is. In this way the enormous differences between the numbers obtained by equally conscientious observers are partially explained; in general we should put most faith in the highest values for the specific gravity or the lowest for the specific volumes, and should recollect that errors of several per-cent are quite possible in both.

There is not much more to be said of the older experiments of Le Royer and Dumas (1821), Herapath (1823), Karsten (1824), and Boullay (1830) than that they established, especially those of the two last named, that the volume of a chemical compound is in general not equal to the sum of the volumes of its components; there is mostly a contraction, but in some cases an expansion occurs. The first regularity in this domain was found by Ammermüller (1840), who noticed that

cuprous and cupric oxides have the same molecular volume if we compare  $\text{Cu}_2\text{O}$  with  $\text{Cu}_2\text{O}_2$ . It is as if one atom of oxygen in the lower oxide occupied as much space as two in the higher. Some other examples also correspond to a similar regularity, but many exceptions were soon found.

The question whether the molecular volume  $\frac{m}{s}$ , where  $m$  is the molecular weight and  $s$  the specific gravity of the substance, could be conceived as in the case of liquids to be an additive property was then carefully investigated by Kopp (1841), and on the whole answered in the affirmative. The molecular volumes are approximately sums of terms depending on the nature of the atoms or atomic groups. These partial volumes are, however, firstly, not always equal to the atomic volumes of the free elements, and secondly the addenda are only constant within somewhat narrow groups, which are for the most part formed of isomorphous compounds (cf. p. 169).

In the closest connection with this relation stands the "parallelism" of isomorphous groups enounced by Schröder (1859). If we arrange analogous salts (*e.g.* the chlorides, bromides, and iodides of the alkali metals and of silver) in a table, in such fashion that compounds of the same element come into one line, vertical or horizontal, then the differences between the molecular volumes of parallel lines will be constant. Thus we find

KCl . 37.4	NaCl . 27.1	AgCl . 25.6
KBr . 44.3	NaBr . 33.8	AgBr . 31.8
KI . 54.0	NaI . 43.5	AgI . 42.0

where all the iodides, for example, have molecular volumes some sixteen units greater than the chlorides, and where the sodium and silver compounds differ by from one to two units irrespective of the other component.

The sulphates, carbonates, and nitrates of barium, lead, and strontium form a similar set, yet, as has been mentioned, the regularity is evidently limited to isomorphous groups.

The question as to the relation in which the atomic volumes of the elements in the free state stand to their atomic volumes in compounds has only been very incompletely answered. From the fact that potassium chloride, for instance, occupies a smaller volume (37.4) than the potassium contained in it (45.2) we see that some elements decrease considerably in volume when they enter into combination. The assumption is made by Schröder that the volume occupied in the compounds is a rational fraction of the atomic volume when any condensation takes place. Some facts may be very well represented by such an assumption, but it is not at present possible to form a clear conception of the statement that a component of a solid occupies a definite volume within it.

If we assume that silver in silver chloride occupies the same volume as it does in the metallic state, viz. 10·3, then there remains 15·3 over for the chlorine; deducting this number from the volumes of potassium and sodium chlorides we get the numbers 22·1 and 11·8 respectively. Now, the volumes of potassium and sodium in the free state are 45·2 and 23·8, which are nearly twice as large as the volumes of the metals in combination calculated on the above assumptions.

Such regularities are limited, however, to small groups of substances. Their extension may be expected when the theory of Frankenheim and Solneke regarding the structure of crystals, has been so far developed as to allow of definite assumptions being made with respect to the particular form of the space net belonging to each crystal and to the nature of the component molecules.

## CHAPTER VII

### OPTICAL PROPERTIES OF SOLIDS

AMORPHOUS bodies do not essentially differ from liquids in respect of their general optical properties. On the other hand quite new phenomena appear with crystals, phenomena having the closest connection with the general properties of symmetry, as Brewster first showed in 1819.

Regular crystals behave optically quite in the same manner as amorphous solids or liquids, a ray of light being so refracted in the plane containing it and the normal to the surface, that a constant ratio is maintained between the sines of the angles of incidence and refraction.

Light moves quite differently in crystals not belonging to the regular system. Fresnel (1831) pointed out that the nature of the medium of the light undulations—the ether—is, in crystals, not the same in all directions. In such a medium every undulation is decomposed into two other mutually independent undulations at right angles to each other, and proceeding along the axes of greatest and least elasticity. Every ray of light, therefore, is in general split up into two when it enters a crystal which does not belong to the regular system. The mathematical investigation of the equations of motion of such a medium has explained theoretically a great number of remarkable optical phenomena in crystals, and has even predicted some previously unobserved, so that, reasoning backwards, the fundamental assumptions made have proved themselves completely suited to the purpose. The principal results are these :—

If we describe a plane containing the axes of greatest and least elasticity, we find that in this plane there are two directions in which the rays move at the same speed. Consequently in these directions, which are called the optical axes, there is no decomposition into two rays. Their position depends on the ratio of the elasticities in the directions of the axes ; they may intersect at any angle, but are always symmetrical with respect to the axes of elasticity, so that the latter bisect the angles made by the optical axes. If the axis of greatest

elasticity bisects the acute angle of the optical axes the crystal is called positive, in the other case it is called negative.

An axis of mean elasticity lies at right angles to the plane of the axes of greatest and least elasticity, and its value serves to complete the specification of the optical properties of the crystal. This mean elasticity can assume all values between the greatest and least elasticity. In the limiting case where it is equal to one or other of these, altogether new properties appear, the two optical axes then coinciding and running in the direction of the third axis of elasticity. Instead of the two optical axes we have therefore only one, and simultaneously all planes passing through this axis become optically equivalent. While in the general case the refracted rays do not remain in the plane of incidence, in the case of optically uniaxial crystals only one ray does not do so; the other follows the usual law of refraction. The former is called the extraordinary, the latter the ordinary ray.

If the elasticity in the direction of the third axis also becomes equal to the others, the motions of the ether are the same in all directions under the same conditions, and no double refraction takes place; the crystal is isotropic, and behaves like an amorphous body.

The three groups of isotropic, optically uniaxial, and optically biaxial crystals agree with the three crystallographic groups of regular crystals, crystals with one principal axis (quadratic and hexagonal), and crystals without a principal axis (rhombic, monosymmetric, and asymmetric). In the rhombic system the axes of elasticity coincide with the crystallographic axes, and the optical axes lie symmetrically with respect to them. In the monosymmetric system two axes of elasticity lie in the plane of symmetry, and the third lies at right angles to it. The two optical axes, therefore, are also in the plane of symmetry, or in a plane perpendicular to it containing the third axis. In the asymmetric system no definite relation exists between the optical and the crystallographic properties.

From these relations we can form a conclusion as to the crystallographic nature of a substance by observing the optical properties of plates cut from its crystals. Light is polarised on passing through doubly refracting plates; if we therefore observe a section of a crystal between two tourmalines or Nicol's prisms, we can at once decide whether it is cut from a regular crystal or not. If the planes of polarisation of the two polarisers are crossed, no light passes through the system when the plate of a regular crystal is brought between them. If the plate is, however, birefringent it decomposes the polarised light from the first polariser into two rays which are in general brought by the second polariser into such interference that coloured light passes through the system. Therefore if a plate appears bright when seen between crossed "Nicol's" or tourmalines it is birefringent.



To distinguish between the different kinds of birefringent crystals it is best to use plates cut perpendicular to an axis of elasticity and to observe them in convergent light.

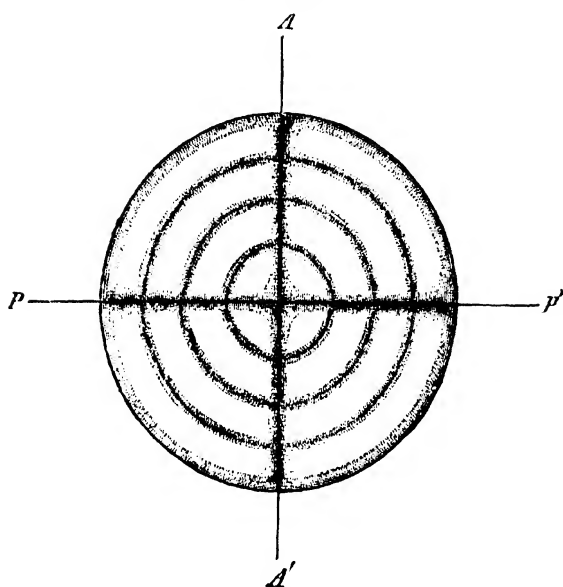


FIG. 39.

We then see coloured figures, the theory of which is completely known but cannot find a place here. Optically uniaxial crystals, when the plates are cut perpendicular to the principal axis, show the coloured rings and black cross of Fig. 39.

Optically biaxial crystals give the forms in Figs. 40 and 41. These can be decomposed into four similar quadrants by two diameters at right angles. With rhombic crystals the rings in the different quadrants are

similarly coloured; with monosymmetric crystals there is a symmetry of the colours with respect to only one of the diameters; with asymmetric crystals the colours are not symmetrical with respect to either of the diameters.

There exist individual exceptions to these general laws; regular crystals in particular often showing double refraction. An explanation of this has been sought in two directions. It has been shown that in many cases there are internal strains in the crystals, causing double refraction; just as this appears in amorphous bodies unequally compressed or expanded.

In other cases the regular form is only apparent; the crystals are actually so composed of biaxial crystals by twin formation that the

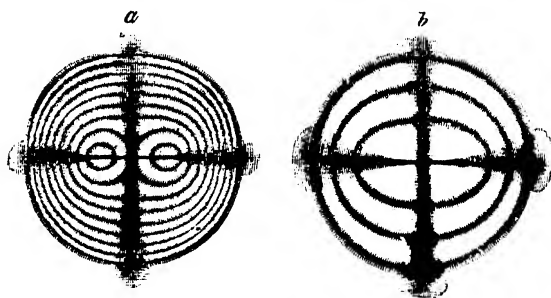


FIG. 40.

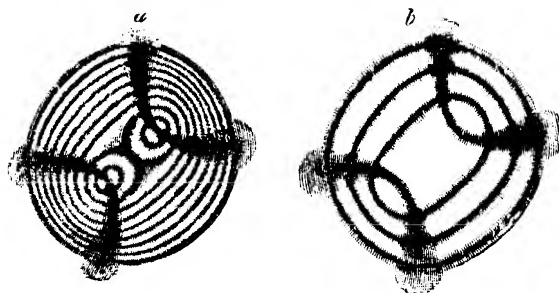


FIG. 41.

external form of a regular crystal is produced. This point, however, is by no means completely cleared up.

A specially interesting relation was discovered by Herschel (1835) between crystalline form and the ability to rotate the plane of polarisation. Quartz crystallises in hexagonal prisms terminated by six-sided pyramids. At the solid angles of the combination there are frequently truncating tetartohedric faces, appearing either on the right or on the left. In complete parallelism with the occurrence of the right and left-handed secondary faces there exists the ability of the quartz to rotate a ray sent in the direction of the optical axis respectively to the right or to the left, so that we can predict the optical properties of a quartz crystal from its external appearance.

This property in the case of quartz is directly connected with the crystalline form; fused quartz is no longer optically active. All other crystals that rotate the plane of polarisation have likewise such asymmetrical secondary faces. If they are not visibly developed on the crystal, the hemihedric or tetartohedric nature of the latter may be made evident by superficial "etching." Sharply defined microscopic figures appear which in the case of regular crystals are symmetrically developed, while the forms just mentioned exhibit figures with one-sided development, either right-handed or left-handed, corresponding to the optical properties.

In these crystals the cause of the rotation of the plane of polarisation must lie in the building up of the molecules, since the ability ceases with the destruction of the crystalline form by fusion or solution. We have already met with substances whose molecules themselves must be correspondingly constructed (p. 103). When such substances crystallise, they show without exception hemihedric or tetartohedric formations, as may be seen if necessary by means of the figures obtained by "etching" with a proper reagent on their faces. If the optical activity disappears, as in the transformation of tartaric into racemic acid, the one-sided development of the crystals of the substance disappears simultaneously.

How the molecules or atoms must be arranged that optical activity may be exhibited appears from an experiment made by Reusch (1869), who piled up a number of plates of mica (optically biaxial) so that the optical principal section of each plate was turned always in the same sense through  $60^\circ$  from the position of that of the preceding plate. Such a pile behaved like a plate of quartz, and was dextro- or levo-rotatory according to the way in which the plates were piled up. A similar spiral arrangement of the particles is therefore probable in crystals or other substances that rotate the plane of polarisation. The theory of crystalline structure on p. 160 admits of numerous arrangements of points in which such a spiral order is produced, and which might therefore serve as types of substances like quartz or sodium chlorate.

## CHAPTER VIII

### SPECIFIC HEAT OF SOLIDS

WHILE engaged in an extensive research on the laws of heat, Dulong and Petit (1818) discovered one of remarkable simplicity which they stated as follows: The atoms of all elements have the same capacity for heat.

In other words, the product of the specific heat and the atomic weight is constant. Or, again, quantities of the different elements in the proportion of their atomic weights are raised through the same temperature by the same quantity of heat.

The importance of the discovery was at once recognised, but doubts were soon raised as to its general applicability, especially as the undoubted analogy between nickel and cobalt was called in question by the numbers obtained. The research was not completed, as Petit died shortly afterwards, and Dulong did not again take up the matter.

F. Neumann (1831) extended the law by applying it to compounds. His mode of statement is this: The specific heats of substances of similar composition are inversely as their molecular weights, or, what is the same thing, quantities of similarly composed substances in the proportion of their molecular weights have the same capacity for heat.

Numerous investigations into this subject were then undertaken by Regnault (1840) and Kopp (1864). These have in the first instance confirmed Dulong and Petit's, and Neumann's laws within wide limits, but have at the same time shown that both are of only an approximate character. The products of specific heat and atomic weight are equal for very many but not for all elements, the numbers often differing from each other by more than the amount of the experimental error.

With respect to the relations between the atomic heats of the elements and those of their compounds, the principle was enounced by Joule in 1844, after assumptions made by Avogadro, Hermann, and Schröder had been proved erroneous, that the specific heat of a com-

pound is the sum of those of its components. To Kopp belongs the credit of having proved this law to be of great generality.

According to him the following elements have a "normal" atomic heat, *i.e.* such a specific heat that when multiplied into the atomic weight gives a number nearly equal to 6.4: Ag, Al, As, Au, Ba, Bi, Br, Ca, Cd, Cl, Co, Cr, Cu, Fe, Hg, I, Ir, K, Li, Mg, Mn, Mo, N, Na, Ni, Os, Pb, Pd, Pt, Rb, Rh, Sb, Se, Sn, Sr, Te, Ti, Tl, W, Zn, Zr.

A smaller atomic heat is possessed by S = 5.4, P = 5.4, F = 5.0, O = 4.0, Si = 3.8, B = 2.7, H = 2.3, C = 1.8 and Be. Only elements of low atomic weight are in this class; those whose atomic weights exceed 30 obey the law of Dulong and Petit.

For several elementary substances it has been proved that the atomic heat increases rapidly with rise of temperature until it attains the "normal" value of somewhat more than 6. Weber found this to be the case for carbon, silicon, and boron, and Nilson and Pettersson for beryllium. Some of the above numbers have not been directly observed, but calculated from the molecular heat of compounds by subtraction of the atomic heats of the other elements.

The question of the theoretical signification of Dulong and Petit's Law still remains to be answered. In this direction we have to leave almost everything to the future. We are evidently precluded from imagining any theory of the solid state analogous to the kinetic theory of gases and thus we lose a valuable guide. We must from the outset have it perfectly clear before us that the specific heat as we ordinarily measure it represents a complicated function of internal and external work, the relative amounts of which are unknown. Attempts to calculate the work done on heating in addition to the mere elevation of the temperature have led to no conclusion, as we are in almost complete ignorance of the decisive constants, in particular the compressibility. Boltzmann, on preliminary approximate assumptions, has estimated the internal work done by the heat to be equal to half the total heat communicated.

With this uncertainty as to the real meaning of the law of Dulong and Petit, it is impossible to state anything with respect to the signification of the deviations from it. We can only note empirically that the law holds good for substances with atomic weights higher than thirty, and may therefore always be applied to such. The law, however, has been of great practical importance, as it was until quite recently almost the only means, besides vapour density and the periodic system, of choosing the correct atomic weight of newly discovered elements from among the different possible values.

# BOOK VI

## CHEMICAL SYSTEMATICS

### CHAPTER I

#### THE CHOICE OF THE ATOMIC WEIGHTS

AFTER the combining-weights of the different elements have been determined (cf. p. 18 *et seq.*) there still remains the question of how to fix the atomic weights. The former are numbers involving no theoretical assumption; that one part of hydrogen combines with eight parts of oxygen, or eight parts of oxygen with three of carbon is simply the expression of our experience, and we merely use a similar expression when we say that the numbers 1, 8, and 3 are the combining-weights of these elements.

But now there comes a difficulty. One part of hydrogen can also combine with sixteen parts of oxygen; and there are, further, compounds that for one part of hydrogen contain six and twelve parts of carbon, while eight parts of oxygen can unite with six parts of carbon as well as with three. With regard to such facts the simple conception of combining, or equivalent weights, as they have also been called, entirely fails, unless we assume for the same element as many different equivalent weights as there are compounds of it with another element, these equivalents being then in simple rational proportions.

It has already been stated (p. 6) that it was owing to precisely this same fact, of two elements being capable of uniting in different proportions, that the atomic hypothesis was advanced. As soon as this is assumed there immediately arises the question of atomic weights.

The atomic weights can either be the equivalent weights of the elements or multiples of them. The first assumption is the simplest, but it gives us no information where we have different compounds of the same elements. In such a case we have as guides to start with, the two principles of simplicity and similarity which were jointly used by Berzelius, the most influential of the early investigators.

The atomic weights were accordingly so determined that the best known and most important compounds received the simplest possible formulæ. The formulæ of substances of similar chemical behaviour were then put into a corresponding form. Iron, for example, gives two oxygen compounds which for fifty-six parts of iron contain sixteen and twenty-four parts of oxygen respectively. The simplest assumption is that in the first oxide equal numbers of iron and oxygen atoms are present, in the second two atoms of iron to every three of oxygen. If we took the atomic ratio 1 : 1 for the second oxide, the first would contain three atoms of iron for every two of oxygen. This seemed less simple to Berzelius, for although the formulæ of the iron compounds themselves would not be rendered more complex, there are a great many other oxides similar to the lower oxide of iron which should therefore, according to the second principle, all contain three atoms of metal to two of oxygen. On the other hand Berzelius gave to alumina the formula  $\text{Al}_2\text{O}_3$ , which, although less simple than the formula  $\text{AlO}$ , and not made necessary by the existence of any other oxides of aluminium, is yet to be preferred on account of the great similarity of alumina in its combinations to ferric oxide.

Such decisions are, however, always subject to personal bias. An objective mode of deciding seemed possible when Gay-Lussac's Law of Volumes was taken into consideration. The idea that the same number of atoms is contained in equal volumes of the elementary gases was at first accepted, but this idea came to grief when compound gases were considered. If chlorine combines with hydrogen without diminution of volume, there must be in one volume of hydrogen chloride only half as many "atoms" as there are in elementary gases. Avogadro, it is true, soon showed that this difficulty may be removed by discriminating between atoms and molecules, but his suggestion remained long unheeded. Only when the distinction was again brought to the front by the development of the molecular conception caused by the acquisition of new facts in organic chemistry, did chemists come back to this way out of the difficulty, and accept it gladly.

Another thing, too, that contributed largely to its acceptance was the proof given by Cannizzaro (1858) that the atomic weights deduced from the vapour densities by the employment of the molecular conception, were, with few exceptions, in accordance with the atomic weights determined by means of the law of Dulong and Petit (p. 176). The concordance is general, if we except the elements with small atomic weight, whose position with respect to the law has already been discussed; the atomic weights of these elements, however, have been ascertained from the densities of their gaseous compounds with such certainty that their exceptional position is of no practical significance, nor indeed has it any theoretical significance as long as Dulong and Petit's Law itself is so little understood.

A third aid to the systematic arrangement of the elements is offered by isomorphism. As isomorphous bodies are in general similarly constituted, we may conversely conclude that similar composition exists where we find isomorphism, and so attain the necessary data for the choice of correct atomic weights.

These three modes lead as a rule to the same results, and have made it possible to exercise an unexceptionable choice from the possible values, a choice which has been in almost every case generally accepted. Other more recently discovered methods have served only to confirm the resulting system of atomic weights.

In the following table will be found a concise statement of the reasons for the choice of the values presently in use for the separate elements:—

Hydrogen,  $H = 1$ , serves as standard.

Oxygen,  $O = 16$ , from the proportion by volume 1:2 with hydrogen on the formation of water; from the equality of its atomic heat with that of hydrogen in the gaseous state.

Nitrogen,  $N = 14$ , from the proportion by volume 1:3 to hydrogen on formation of ammonia, and to oxygen in the corresponding compounds; from the equality of its atomic heat with that of gaseous oxygen and hydrogen.

Carbon,  $C = 12$ . From the vapour densities of both organic and inorganic compounds there has never been found a smaller molecular weight than corresponds to  $C = 12$ . The specific heat gives no definite information.

Chlorine,  $Cl = 35.46$ . From the proportion by volume 1:1 on combination with hydrogen; from the volumes of the chlorine compounds.

Bromine,  $Br = 79.96$ , and Iodine,  $I = 126.86$ , are perfectly analogous to chlorine in their compounds, as well as isomorphous with it.

Fluorine,  $F = 19.0$  is with some uncertainty determined from the analogy with the chlorine compounds.

Sulphur,  $S = 32.06$ , from the vapour density, the volume of hydrogen sulphide, and from the specific heat.

Selenium,  $Se = 79.1$ , is isomorphous and analogous to sulphur.

Tellurium,  $Te = 125$ , is isomorphous and analogous to sulphur and selenium.

Phosphorus,  $P = 31.0$ , from the specific heat (somewhat uncertain). From the vapour density of the element itself we should conclude that it possessed double this atomic weight, but the vapour density of hydrogen phosphide, on the other hand, gives  $P = 31$ .

Arsenic,  $As = 75$ , from the specific heat, the vapour density of the trichloride, and the isomorphism with phosphorus.

Silicon,  $Si = 28.4$ . The specific heat yields uncertain information: from the vapour density of the tetrachloride, and from the isomorphism with titanium and zirconium.

Boron,  $B = 11.0$ , from its volatile compounds.

Lithium,  $Li = 7.03$ , from the specific heat, which is normal notwithstanding the low atomic weight.

Sodium,  $Na = 23.06$  }  
Potassium,  $K = 39.14$  } from the specific heat.

Rubidium,  $Rb = 85.4$ , is isomorphous with potassium.

Cæsium,  $Cs = 132.9$ , is isomorphous with potassium and rubidium.

Beryllium,  $Be = 9.10$ . This element has caused much trouble. Corresponding to the low atomic weight, the specific heat is very small, and an indubitable isomorphism has not yet been shown to exist. A determination of the vapour density of beryllium chloride has decided the question.

Magnesium,  $Mg = 24.38$  }  
Calcium,  $Ca = 40.0$  } from the specific heat.

Strontium,  $Sr = 87.5$  is isomorphous with calcium and lead.

Barium,  $Ba = 137.0$ , is isomorphous with calcium, strontium, and lead.

Aluminium,  $Al = 27$ , from the vapour density of the chloride and from the specific heat.

Gallium,  $Ga = 69.9$ . The vapour density of volatile compounds, the specific heat, and isomorphism all lead to the same value.

Scandium,  $Sc = 44.1$ , from isomorphism with aluminium.

Cerium,  $Ce = 140$  }  
Lanthanum,  $La = 138.5$  } from the specific heat.  
Didymium,  $Di = 140 (?)$  }

Yttrium, Ytterbium, and the other metals of the rare earths, from analogy and isomorphism with cerium, lanthanum, and didymium.

Iron,  $Fe = 56.0$ , from the vapour density of the trichloride, the specific heat, and its isomorphism with calcium.

Cobalt,  $Co = 59$  } from the specific heat and the isomorphism  
Nickel,  $Ni = 59$  } with iron, etc.

Zinc,  $Zn = 65.5$ , from the specific heat, isomorphism with magnesium, and the vapour density of the metal and its chloride.

Cadmium,  $Cd = 112.1$ , from the specific heat and vapour density.

Copper,  $Cu = 63.3$ , from the specific heat and isomorphism with iron, etc.

Silver,  $Ag = 107.9$ , from the specific heat, and isomorphism with sodium.

Mercury,  $Hg = 200$ , from the specific heat, and the vapour density of the metal and its halogen compounds.

Lead,  $Pb = 206.9$ , from the specific heat and the vapour density of the chloride: also isomorphous with calcium, etc.

Thallium,  $Tl = 204.1$ , from the specific heat, the isomorphism with potassium, cæsium, rubidium, and from the vapour density of the monochloride.



Titanium,  $Ti = 48.1$ , from the vapour density of the chloride and the isomorphism with silicon and tin.

Zirconium,  $Zr = 90.7$ , from the vapour density of the chloride and the isomorphism with silicon, titanium, and tin.

Tin,  $Sn = 118.1$ , from the specific heat, the vapour density of the chloride, and the isomorphism with silicon, titanium, and zirconium.

Thorium,  $Th = 232.4$ , from the specific heat and the isomorphism with zirconium.

Vanadium,  $Vd = 51.2$ , from the vapour density of the chloride and oxychloride and the isomorphism with phosphorus and arsenic.

Niobium,  $Nb = 94.2$ , from the vapour density of the chlorides and oxychlorides.

Tantalum,  $Ta = 182.8$ , from the vapour density of the volatile chlorine compounds.

Antimony,  $Sb = 120.3$ , from the specific heat, the vapour density of the chloride, etc., and the analogy to arsenic.

Bismuth,  $Bi = 208.0$ , from the specific heat, the vapour density of the chloride, and the analogy to arsenic and antimony.

Chromium,  $Cr = 52.3$ , from the specific heat, the vapour density of volatile compounds, and the isomorphism with iron, sulphur, etc.

Molybdenum,  $Mo = 95.9$ , from the specific heat (doubtful), the vapour density of volatile compounds, and the isomorphism with chromium.

Tungsten,  $W = 184.0$ , from the specific heat, the vapour density of the chlorine compounds, and the analogy with chromium and molybdenum.

Uranium,  $U = 239.4$ , from the specific heat, the vapour density of the halogen compounds, and the analogy with chromium, etc.

Gold,	$Au = 197.2$	} from the specific heat.
Platinum,	$Pt = 194.8$	
Iridium,	$Ir = 193.2$	
Osmium,	$Os = 192$	
Palladium,	$Pd = 106$	
Rhodium	$Rh = 103$	
Ruthenium,	$Ru = 103.8$	

In this table only the most important data are collected; a large number of other confirmatory relations have been left without mention.

## CHAPTER II

### THE PERIODIC LAW

THE most striking confirmation of the propriety of the above selection of atomic weights is formed by the regularities appearing when the elements are arranged according to the magnitude of the atomic weights so chosen. The relations have been already shortly indicated (p. 35), and now form a fourth and very important means of determining the true from amongst the possible atomic weights, having given a decisive answer in many cases where the other methods failed or were ambiguous.

To complete what has been already said with regard to them, we shall now consider a few properties of the elements and of their compounds in their relation to the periodic system. Besides the discoverers (Meyer and Mendelejeff), Carnelley in particular has instituted investigations in this direction, and at present it may be said that almost every well-defined and comparable property appears as a periodic function of the atomic weight.

As to the chemical properties, all that is needful has already been stated. Of the physical properties of the elements, the atomic volume shows the periodic variation most clearly, as was first indicated by Lothar Meyer. In Fig. 42 the atomic weights are the abscissæ, and the atomic volumes the ordinates, the points being connected by thick lines. As we see, the curve appears as a series of undulations always growing larger as the atomic weight increases, and exhibits the periodicity in the most marked manner. The elements with similar chemical properties are found at similar portions of the curve; thus the strongly basic alkali metals are always at the maximum points, while immediately before them on the ascending portions the strongly acid-forming halogens find their place. After them, on the descending portions of the curve, lie the metals of the alkaline earths, the metals of the earths, and so on, always with diminishing basicity, while the ascending parts are occupied by the elements with a more acid-forming character.

A second property of equally pronounced periodic character is the

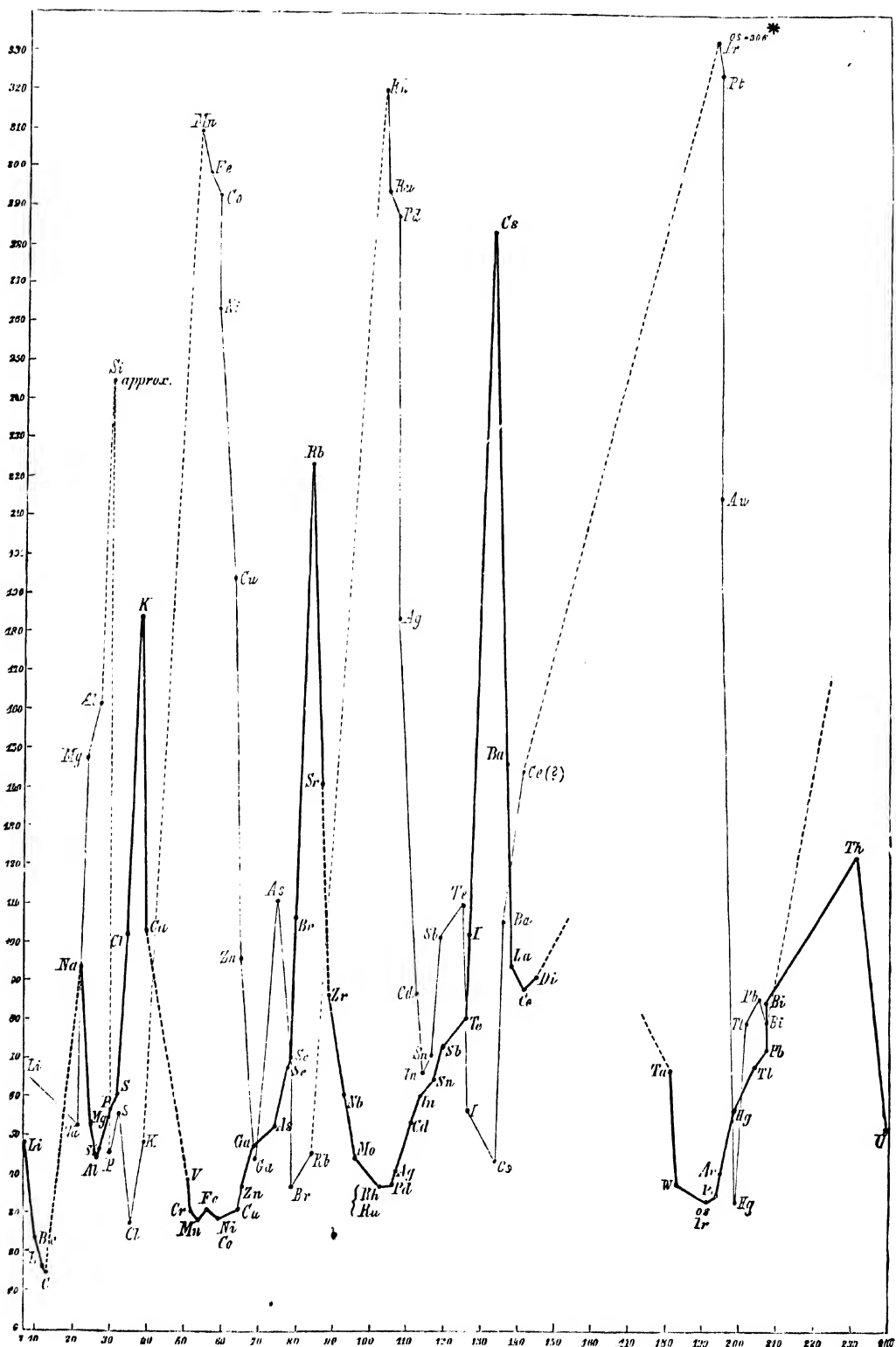


FIG. 42.

The thick line denotes atomic volumes, the thin line melting-points in the absolute scale. The ordinates of the atomic volumes are multiplied by four, the ordinates of the melting-points divided by seven.

\* This point should lie 66 divisions higher.

melting-point. The corresponding curve is given in Fig. 42 by the thin lines. The undulations are here nearly midway between those of the atomic volume, and show a double periodicity, being alternately large and small.

Further regularities of a periodic nature have been observed with the following properties :—molecular volume of the oxides (Brauner and Watts, 1881), refractive power, heat of formation of the chlorides, bromides, iodides, etc., conductivity for heat and electricity, colour, etc. It is unnecessary to enter further into these relations, as the regularities have for the most part no general character as yet, and nothing new is to be learnt from them.

It must also be emphasised that the regularities, so far as they are known, are far from having the sharpness and definiteness desirable. They are not of such a character that one can calculate the properties of an element from those of its neighbours; a rough estimate only can be formed. This of course in nowise diminishes the value of the general principle; it only renders evident that important problems are here still awaiting their solution.

Such a problem is the obvious attachment of certain elements to different groups. Thus chromium, from its decidedly basic monoxide, should go with zinc and magnesium; from its alum-forming sesquioxide, with aluminium and gallium; while from its acid-forming oxide it ought to be classed with molybdenum and tungsten: only the last analogy has found a representation in Fig. 42. Copper, by its lower oxide and its insoluble lower chloride, is doubtless related to silver, but mercury from the next group and thallium from the third are much more nearly allied to these metals than sodium or gold; while, on the other hand, cupric oxide would serve to place copper along with magnesium and zinc. Manganese, corresponding to its different degrees of oxidation ( $\text{MnO}$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{MnO}_2$ ,  $\text{MnO}_3$ , and  $\text{Mn}_2\text{O}_7$ ), could be brought into five distinct groups. For these and numerous other facts no expression is given by the periodic system.

It must be further borne in mind that the elements with lowest atomic weight have quite an abnormal character. Mendelejeff has called these the "typical elements," a name signifying just the opposite of what is really meant, for these elements are by no means typical of the groups whose first members they constitute, but rather show a decided tendency to assume the properties characteristic of the next following groups. Lithium, for instance, forms a sparingly soluble carbonate and an easily soluble bicarbonate, thus resembling the bivalent metals of the alkaline earths, and not the metals of the alkalis. Beryllium in its behaviour is so like aluminium that until the determination of the vapour density of its chloride it was considered by many chemists as a trivalent element. Trivalent boron, again, in the free state as well as in its compounds, is like no other element so much as quadrivalent silicon. Fluorine is distinguished by forming compounds in which it behaves like a bivalent element.

The periodic law is once more unable to give a rational explanation of these peculiarities.

The differences between the progressive numerical values of the atomic weights are by no means the same, but vary as much as cent per cent. This is the case with elements whose atomic weights have been so exactly determined that the hope of later researches bringing the values to equal distances apart cannot be entertained. It may, however, be possible to bring these irregularities into a relation of mutual dependence with others known to exist, and so discover a law regulating them. The periodic system leaves at present the impression that the elements are somewhat irregularly scattered in a regular scheme, so that they in some way do not quite fall into their proper places.

In spite of all this, however, we must not hesitate to acknowledge that the discovery of the properties of the elements and of their comparable compounds being periodic functions of their atomic weights, is one of the most important steps made by scientific chemistry in late times. The principle has stood the test both in the prediction of the properties of elements at the time undiscovered, and in the indication of errors in the atomic weights previously accepted. We must again emphasise the intimate connection between the periodic system and the other grounds for the choice of the real atomic weights. Every attempt to find similar relations in other systems of atomic weights—Gmelin's "equivalents," for example—has proved abortive, so that the periodic law stands, as a means of determining the true atomic weights, on an equal footing with isomorphism, the law of Dulong and Petit, and the law of Avogadro.

## CHAPTER III

### THE MOLECULAR THEORY

IN discussing the properties of substances separately, we have repeatedly adverted to their threefold character. Some properties suffer no change through the process of chemical combination; they are entirely independent of the state of the element, and their values in compounds are, therefore, equal to the sums of the corresponding values in the component elements. These are the additive properties, the most striking example being mass, which through all chemical change remains constant. The specific heat too is essentially additive; and molecular volume and molecular refraction have also in the main an additive character—here, however, the properties of the elements do not always enter into those of the compounds with the same value, but assume a number of different values according to the chemical function the elements perform.

Quite different from these properties are those which we have called colligative (p. 58). They always retain the same value for certain complexes without regard to the more or less composite nature of these; of a summation there is here no trace.

While the additive properties have given rise to the atomic theory—*i.e.* the assumption that in chemical compounds the elements exist as such, in particular with unchanged mass—the colligative properties have drawn attention to the complexes for which the properties in question assume equal values, and thus have led to the molecular theory. At the foundation of this there lies, as has already been explained (p. 58), the assumption that substances, as known to us, are composed of definite and like groups of constituent atoms, a more intimate union existing between the atoms within these groups or molecules than between the molecules themselves. The colligative properties appear whenever these proximate components of matter act in virtue of their number and not of their nature.

The first and best known case of this is the volume of gases. It has been shown above (p. 64) how the best and clearest hypothesis as to the nature of the gaseous state, the kinetic theory, of necessity

leads to the conclusion that, under the same conditions, there is in equal volumes of gases the same number of molecules. We may confidently predict that any future hypothesis as to the nature of gases, however greatly it may differ from the present one, will still be in agreement with it in this particular point.

It is not only the physical behaviour of gases, however, that has made the assumption of the molecular theory seem expedient. Formerly, when it appeared a matter of course to assume the existence of single atoms of the elements in gaseous oxygen and hydrogen, there was no answer to the question why the two gases should not immediately combine to form water when they are mixed. In the same way, the activity of the elements at the moment of liberation -- in the "nascent" state -- so different from their ordinary chemical activity, remained a fact no less remarkable than inexplicable. Nowadays, when there is ascribed to the "free" elements a molecular state in which, generally speaking, two or more atoms are united to each other, both these facts and many others related to them find a satisfactory explanation. When oxygen and hydrogen are to combine chemically, the work of separating the two atoms in the molecule has first to be done before the liberated atoms can seek new positions of equilibrium. If the atoms, on the other hand, are separated as such in chemical processes, *e.g.* in the action of sodium on water ( $\text{Na} + \text{H}_2\text{O} = \text{NaOH} + \text{H}$ ), this work has not to be performed, so that the liberated atoms can freely exert their chemical affinity on other atoms or atomic groups in their neighbourhood. This is what we call the nascent state.

The molecular conception, finally, has proved to be exceedingly useful in systematising the organic compounds, having become of the utmost importance for the comprehension of the mutual relations of these bodies, composed of but few elements in the most varied proportions. As, in the choice of the atomic weights, it was first attempted to carry out systematically the principle of equivalents, which slowly yielded to the present system only after the law of multiple proportions had again and again blocked the way, so in organic chemistry the simplest formulæ alone were at first employed. Not before Graham's and Liebig's investigations on polybasic acids, Williamson's classical proof that two alcohol radicals are contained in the ethers, and Gerhardt and Laurent's demonstration that a comprehensive and consistent system of the organic compounds was possible by referring the formulæ to equal volumes in the gaseous state, did the molecular theory finally force its way into chemistry. It was at last accepted by all chemists (with the exception of an ultra-conservative school in France) when Cannizzaro proved that the assumptions necessarily made by the molecular theory were in perfect agreement with the results obtained from the law of Dulong and Petit.

The present task of special chemistry, as will be explained in the next chapter, is to determine the constitution of chemical compounds. After the chemical composition and the empirical formula have been

fixed, *i.e.* the simplest number of atoms which will represent the proportions obtained, the first step towards accomplishing this task is the determination of the molecular weight. Until a short time ago there was only one means of ascertaining this, *viz.* by determining the vapour density. This means could evidently only be applied to volatile substances, and was often therefore useless.

We see, however, at once that the problem can be solved by measuring any colligative property, for all colligative properties assume the same value for equimolecular quantities of different substances. If we thus determine how much of the substance with unknown molecular weight is required to give a value of any colligative property equal to that given by a known quantity of a substance of known molecular weight, then these quantities must be in the ratio of the two molecular weights.

Colligative properties are only known in gases and solutions; they have not hitherto been observed in pure liquids. This is quite comprehensible, for properties conditioned solely by the number, and not by the nature of the independently existing complexes, can only be observed under conditions where the special properties of the complexes or molecules are dormant. The first condition is evidently that the molecules be separated by a sufficiently large distance, a state only realised in gases and solutions. We have consequently no prospect of ever meeting with colligative properties under other conditions. By this is not meant that the determination of the molecular weights of pure liquid substances will always remain impossible. We may come to know them, only we must employ for this purpose properties not colligative.

To determine the molecular weights of dissolved substances the colligative properties discussed on pp. 127-140 may all serve,—thus, the osmotic pressure, the lowering of the vapour pressure and of the freezing-point. The last-mentioned is now experimentally most developed; a determination of the molecular weight by a depression of the freezing-point is much easier and more rapid in the execution than a vapour-density determination, for example.

The question here arises, in what proportion the molecular weights determined according to the different methods stand to each other, in particular whether they are identical. A somewhat comprehensive investigation undertaken by Beckmann (1888) showed that the results obtained by the method of freezing-point depression are in close agreement with those obtained from the vapour density. In one or two cases, where a tendency towards the formation of double molecules is seen in the vapour density, *e.g.* acetic acid, it appeared that different solvents act differently. Dissolved in water, acetic acid exists as normal molecules  $C_2H_4O_2$ , in benzene, on the other hand, it forms double molecules. The water therefore acts on acetic acid like a high temperature, the benzene like a low temperature. Again, for non-volatile substances, whose molecular weights had hitherto only



been inferred from the chemical reactions into which they entered, the values obtained from the depression of the freezing-point were almost without exception identical with those obtained on chemical grounds, so that the method holds good on all sides. It should be observed that when a tendency to the formation of double molecules is present, as it is in many compounds containing hydroxyl, effect is much more completely given to this tendency in benzene solutions than when the substance is dissolved in water, acetic acid, or phenol.

By the discovery of the colligative character of the properties of solutions just mentioned, the possibility of determining the molecular weights, formerly confined to volatile substances, has been enormously increased, for now it extends to all soluble substances, *i.e.* to almost all that come into the chemist's hands. We see at once how much the investigation of unknown substances is advanced by this. If the molecular weight of a new body is known, the possibilities of its rational constitution suffer an immediate and great limitation, so that a choice is materially facilitated.

Little is as yet known concerning the molecular weights of pure liquid substances. Many chemists are inclined to assume that the liquid molecules are composed of a comparatively large number of gas molecules, so that if  $M$  denotes the gas molecule, the liquid molecule would be represented by  $(M)_n$ . This is undoubtedly the case with bodies such as acetic acid where the tendency to the formation of double molecules is already present; liquid acetic acid very probably consists of molecules having the formula  $(C_2H_4O_2)_2$ . With other liquids where this tendency does not exist in the vapour there is no ground for assuming such complex molecules, and we shall always come nearest the truth, as far as our present knowledge of the subject goes, by supposing the molecules of the liquid to have the same composition as those of the vapour. In one case we might seem to have a direct proof of this assumption, namely, in the vapour pressure of solutions. As the vapour pressure (p. 132) depends on the number of molecules of the dissolved body and of the solvent, there is apparently a method offered for determining the molecular weight of the one substance when that of the other is known. Such a conclusion is not, however, justified, for in this case only the number of molecules leaving the liquid to become vapour is taken into consideration, and not those which remain in the liquid.

The molecular weight of solids still remains an unsolved problem. The only thing that can be said with any degree of certainty is that the molecules are probably of a comparatively complex character. Sulphur, even as a gas, contains at temperatures below a bright red heat six atoms in the molecule, as a liquid and a solid certainly not less. The fact that several elements can exist in so extraordinarily different allotropic forms as carbon in charcoal, graphite, and diamond, or phosphorus in the red and yellow modifications, cannot in the light of the molecular theory be otherwise interpreted

than by the assumption of more or less composite molecules in the various forms.

When allotropic solids are brought into the liquid or gaseous state, not a trace of difference between them is left. The vapour of red phosphorus is identical with the vapour of yellow phosphorus, and a solution of rhombic sulphur in carbon disulphide is in no respect different from a solution of similar composition made from monosymmetric sulphur. Conversely, from the same solution, *e.g.* one of nickel sulphate supersaturated by cooling, any one of the different forms of the salt may be obtained by the introduction of a fragment of the corresponding crystal. The so-called physical isomerism thus occurs exclusively in connection with the solid substance, and disappears whenever the latter assumes another state of aggregation.

For these reasons the attempts frequently made to deduce the crystalline form of chemical compounds from their elementary composition have all proved fruitless. The crystalline particles are obviously only in exceptional cases identical with the molecules.

## CHAPTER IV

### THEORY OF CHEMICAL COMPOUNDS

OF the numerous questions concerning the nature of chemical compounds, Dalton's atomic hypothesis only answered one, that, namely, which asked whether or not the elements exist as such within them. The answer was affirmative. Chemical compounds are complexes formed by the conjunction of elementary atoms. The facts and theories in the first two chapters of Book V. gave us information as to the relative mass of the atoms; the molecular theory and the observations on which it is founded made us in certain definite cases cognisant of the number of atoms in such complexes. In the present chapter we shall be occupied by the mutual relations of the atoms within the molecule.

This problem is of course purely hypothetical, for the existence of the atoms themselves is only a hypothesis. But based on this hypothesis a theory of great fertility has been developed, and—apart from metaphysical scruples about the atomic theory, which for the most part rest on misapprehension—there lies in the results already obtained a guarantee that further advancement of the theory will lead to results equally serviceable. This advance may not be made by assuming any arbitrary forces and properties, but must come directly from the fundamental assumption that the atoms are finite, and, for the same element, similar bodies. But as every finite quantity of matter occupies a position in space which is definable with regard to other material particles, the question as to the relative position (or motion) of the atoms in the molecule is scientifically justified, and must be put sooner or later by the atomic theory.

As a matter of fact the question is as old as the theory itself; from the time that compounds were conceived as being composed of atoms, chemists have endeavoured to obtain a clear idea of the mutual relations of these components.

The first theory of chemical compounds is due, as we know, to Berzelius, who founded it on the phenomena observed by him during the electrolysis of salts. He saw that the acids of the salts of the alkalies (chiefly studied by him) collected at the copper pole and the

bases at the zinc pole, and so, according to the old principle of Stahl, that a body consisted of those things which by their union gave it, and which on its decomposition were re-formed, he concluded that acids and bases were the components of the salts. The known acids and bases on their combination always produced water in addition, but this was supposed to be pre-existent in them, playing the part of a base in the acids, and of an acid in the bases; the real acids and bases were the known substances minus this water.

The same principle was at once extended to all other groups of bodies. Oxides too could be decomposed electrolytically, giving on the one hand oxygen, on the other a metal. Berzelius therefore looked upon compounds quite generally as being formed of two parts which were held together by electrical attraction, and could be separated by electrical forces. In this way arose the electrochemical system, according to which the binary arrangement holds good step by step in the most complicated compounds. Alum, for example, was supposed to consist in the first instance of potassium aluminium sulphate and water; the latter was a binary compound of oxygen and hydrogen, the former of aluminium sulphate and potassium sulphate. Each of these salts again consisted of sulphuric acid ( $\text{SO}_3$ ) and a metallic oxide, and these two components finally were composed of oxygen on the one hand, and sulphur or a metal on the other.

This view, in principle so clear and simple, proved exceedingly useful although its foundation was false. Potassium sulphate, as we now know, splits up on electrolysis, not into  $\text{K}_2\text{O} + \text{SO}_3$ , but into  $\text{K}_2 + \text{SO}_4$ , and the principle of the dualistic theory of Berzelius, that only compounds of the same order can unite to form higher compounds, is contradictory to the fundamental phenomenon from which it was deduced.

In spite of this fundamental error, the electrochemical theory has been of the greatest importance in the development of chemical science. By giving a list of substances arranged according to their electrochemical tension, Berzelius laid the foundation of the science of comparative affinity; while the easily understood and rigorous system rendered possible by the theory has eminently advanced the study of chemistry. Even after the discovery of the error contained in the conception of the process of electrolysis, the theory did not fall to the ground, but remained until its inapplicability to a class of compounds not known at the time of its development was made evident. This class is formed by the non-electrolysible organic compounds.

The electrochemical theory had not much to do with the "topography of the atoms." Beyond the assumption that in the oxygen-salts a part of the oxygen is contained in the base and a part in the acid, it scarcely required any other. It should only be mentioned that according to this theory each complicated compound was composed of atoms and groups of atoms held together by gradually weakening bonds, so that the binary members within the complex through their more powerful internal connection led a

sort of isolated and independent existence. Here we see the germs of the later developed theory of radicals.

An earnest consideration of the relative position of the atoms in the molecule only became requisite when facts were made known that could not be otherwise explained by the atomic theory than through different arrangement of the atoms. This is what is called isomerism.

When Wöhler in 1823 analysed cyanic acid, and Liebig in 1824 fulminic acid, it was discovered that both chemists had found the same composition for these undoubtedly different substances. Berzelius, who compared the researches in his *Jahresbericht* indulged in several speculations as to the manner in which one or other of the investigators could have fallen into error, for that two so different substances could have the same composition appeared to such a degree unlikely that the possibility was never entertained.

However, in the following year, Faraday in the course of an investigation of the hydrocarbons which had collected in cylinders used for compressing coal-gas, found besides benzene, a gas (butylene) having the same composition as the well-known olefiant gas (ethylene), but twice as great a specific gravity in the gaseous state. Berzelius familiarised himself gradually with the idea that in reality substances of the same composition could have different properties, and called attention in his turn to the two distinct stannic oxides. Almost every year now added to the number of new substances of the same composition with different properties, until finally in 1830 the racemic acid discovered by Kestner proved to be in every respect similarly composed to ordinary tartaric acid, although in its solubility, the crystalline form of its salts, and in its reactions it differed indubitably from the latter.

Berzelius then made the recognition of identically composed substances with different properties the general possession of science by giving it the name isomerism. He soon too distinguished between different kinds of this; for such compounds as Faraday's hydrocarbons, which contained the same elements in the same proportions, but a different number (multiple) of atoms, he introduced the name polymeric, while such substances as contained the same number of atoms merely differently "arranged," he called metameric. These very suitable names remain in use at the present day.

The fact of the existence of isomerism has been of the greatest significance for the theoretical form taken by chemistry, for from it followed that not only the number and nature of the component atoms were of decisive influence in what concerned the properties of a compound, but that there was something besides—something hypothetically referred by Berzelius to the atoms being "placed together in different ways." This view was retained in the whole of the coming

development of the conception of isomerism, and at first took the form of the assumption of different "radicals" in the compounds. The assumption, it is true, was not made to explain the phenomena of isomerism; quite other facts caused this development of the electrochemical doctrine, but many cases of isomerism could be conveniently explained by the difference of the radicals.

During the great research of Liebig and Wöhler on benzoyl (1832), a number of substances came to be known which all contained the atomic complex  $C_7H_5O$ , and were derived from the same original material. A special rôle within the compounds was credited to this unchanged portion; its atoms were supposed to be held together by stronger forces than those which bound the variable components. Here was the theory of radicals; those more stable complexes played the same part in complex compounds as the elements in simpler compounds; Liebig even went the length of stating that these radicals were the true elements of organic chemistry. By the heroic investigations of Bunsen on cacodyle, and the supposed isolation of ethyl by Frankland, so much was adduced in favour of the theory of radicals, that it generally came to be considered the only true form for the conception and representation of the nature of chemical compounds.

The want of clearness in the theory as to the character of the stronger or closer binding of the atoms within the radical, and as to how far this differed from the binding of the radicals amongst themselves or with other atoms, was at that time not felt, because then the problems of chemical affinity never entered into any one's mind at all. Indeed, several chemists, following the example of Berzelius, expressly assumed the existence of a special sort of union different from the ordinary kind, and this they distinguished as "pairing" or "coupling."

While the theory of radicals grew out of the electrochemical theory, and merely applied its fundamental conceptions without alteration to the new units, another mode of viewing the facts came more and more to the front, and was always receiving fresh support. It was advanced by Laurent (1839), alternately taken up and dropped by Dumas, and fiercely combated by Berzelius, although it finally proved to be perfectly justified and in the highest degree fertile. This was the idea of substitution, the notion that single atoms in a compound could be replaced by others, the new substance still remaining analogous to the original compound. Such observations were first made on the action of chlorine upon organic compounds containing hydrogen; a particularly pregnant example being found in trichloroacetic acid (discovered by Dumas), in which three hydrogen atoms of the acetic acid were replaced by three chlorine atoms. The close relationship of this acid to acetic acid was especially noticeable in its retransformation into the latter, a reaction discovered by Melsens.

The new theory contradicted the electrochemical theory in two great points. Berzelius could not admit that "electropositive" hydrogen was so replaceable by "electronegative" chlorine that the similarity of the two

compounds could be preserved. On the other hand, the assumption of a substitution—of the entrance of one atom into the place of another, was in direct contradiction to the electrochemical principle of binary arrangement. Both these points were energetically emphasised by the upholders of the theory of substitution. The first led to the proposition, that the “position” alone of an atom—not its nature—was of influence on the properties of the compound. In this form the proposition is certainly not true, and at once experienced opposition. A. W. Hofmann was soon able to show from the bromine substitution products of aniline, that according to the position of the bromine its properties frequently appeared very much weakened in their influence, although they never disappeared altogether.

While a compromise could here be made between the new and the old views, the idea of the unitary constitution of chemical compounds obtained a complete victory over the binary constitution. This reform was in agreement with the conception of the molecule as described above, and led to the setting up of molecular schemes, the chemical types, which we shall shortly consider more closely.

The law of substitution meanwhile was more and more extended. It was recognised that not only chlorine, bromine, and iodine could replace the hydrogen of organic compounds, but that compound radicals possessed the same property. Here the radicals of the old theory are represented as the true substituents, as was especially perceived by Hofmann and Wurtz from their study of the substituted ammonias. At the same time the way was prepared for the distinction between atom and equivalent: one atom of oxygen does not replace one but two atoms of hydrogen on substitution, and has therefore twice the substituting value of the latter.

Dumas, on taking up the idea of substitution, soon carried it, as was his wont, to its extreme consequences, assuming that only the arrangement, and not the nature of the atoms, determined the properties of the compounds. The task therefore of finding the principal types lay immediately before him. His attempt to fix them was, however, unsuccessful.

It was the later researches of Williamson on the ethers, and of Hofmann and Wurtz on the organic ammonias, that enabled Gerhardt and Laurent to put the idea into a practical form. According to them all compounds were derived from the types of hydrogen  $\begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \}$ ,

hydrochloric acid  $\begin{smallmatrix} \text{H} \\ \text{Cl} \end{smallmatrix} \}$ , water  $\begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \}$  O and ammonia  $\begin{smallmatrix} \text{H} \\ \text{H} \\ \text{H} \end{smallmatrix} \}$  N, by the re-

placement of their hydrogen atoms by other elements or radicals. To this scheme Williamson added that of the double and triple “condensed” types, and Kekulé introduced “mixed” types formed by uniting two or more different simple types. In these last attempts to bring the schemes into harmony with the facts, we already find a factor

which later on became of great importance. In order that the two groups in condensed or mixed types might be held together, an atom or radical had of necessity to be present which could take the place of two hydrogen atoms, and which thus formed the connecting link, one hydrogen atom in each group being replaced by it. Here, then, there appeared for the first time the conception of the polyatomic radical or element as the condition for the holding together of the molecule.

The classification of compounds according to types was of the greatest use to science, for it gave a convenient survey of a large number of substances already known, and indicated methods for preparing new bodies. Nevertheless it was, on account of its purely formal character, no real theory of chemical compounds. Gerhardt, its founder, was quite clear on this point; he again and again reiterated that his formulæ were only to be looked on as functional, not as constitutional. Soon too the theory proved unequal to the task of keeping up with the progress of science.

The system of types was by no means generally accepted, for the chief representatives of the theory of radicals (who admitted the law of substitution, and by its means widened the old views) kept strictly aloof from it. In particular, Frankland and Kolbe sought to arrive at a proper understanding of chemical compounds in quite another way, which took better into account the nature of the elements and the analogies with inorganic compounds. Thus Kolbe was in a position to predict the existence of isomers amongst the alcohols, where in the system of types there was only room for one substance; and not only did he prognosticate their existence, but also their behaviour. A few years later Friedel discovered secondary propyl alcohol and confirmed Kolbe's prediction.

A case of isomerism had thus again shown the necessity of going deeper into the problem of chemical constitution. The guiding idea was found by Frankland. In the course of his researches on organo-metallic compounds (1852) he observed that one atom of zinc, arsenic, antimony, etc., had its combining tendency always satisfied by a definite number of univalent elements or radicals, of whatever kind these might be. In this way was laid the foundation for the study of valency or the capacity of saturation of the atoms.

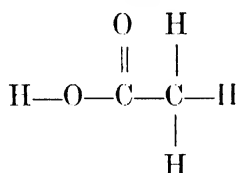
The application to carbon compounds was not made by Frankland. This important step was taken almost simultaneously (1858) by Couper and Kekulé, who perceived that carbon was quadrivalent, and showed that the constitution of numerous carbon compounds could be explained on this assumption. Every carbon atom can unite with four other univalent atoms or radicals (*i.e.* such as can replace one atom of hydrogen), but not with more. We have chiefly to thank Kekulé for carrying through this idea.

In the theory of valency, which is at the present time the prevalent one, there is thus assumed that each atom possesses a definite limited capacity for combining with other atoms. This capacity is called the valency, and the atoms that can combine with one, two, three, four



hydrogen atoms (or equivalent atoms or radicals) are said to be univalent, bivalent, trivalent, quadrivalent, respectively. Carbon is quadrivalent on account of the compound  $\text{CH}_4$ , oxygen bivalent owing to the compound  $\text{OH}_2$ . In general, chemical compounds are so constituted that the valencies of the different elements exactly satisfy each other. In acetic acid, whose rational formula is  $\text{HO}\cdot\text{CO}\cdot\text{CH}_3$ , one of the carbon atoms is united in the first place to a bivalent oxygen atom with two valencies. The third valency is united with one of the valencies of another oxygen atom, whose second valency is satisfied by a hydrogen atom. Lastly, the fourth valency of the original carbon atom is united with one valency of a second carbon atom, whose three others are satisfied by three hydrogen atoms.

These relations may be made clear by the adoption of Couper's idea of affixing to the elementary symbols so many short lines as there are active valencies, and then joining these from atom to atom. Acetic acid would thus receive the following structural formula:—



Such a formula is capable of rendering evident a great many different relations. It shows that one of the hydrogen atoms behaves differently from the others, because it is united with oxygen to form hydroxyl, while the others are all united to carbon. Further, the two oxygen atoms behave differently, the hydroxyl oxygen being more easily attacked and removed than the other. Lastly, the two carbon atoms have different functions: the one, united to two oxygen atoms, easily passes into carbonic acid, the other splits off as methyl,  $\text{CH}_3$ . All these relations just derived from the formula exist in fact; the structural formulæ thus fulfil in a high degree the claim of being both functional and constitutional formulæ.

Now, as to the meaning of such formulæ, there are two things which must be carefully kept distinct—on the one hand, the chemical valency, on the other, its representation by the so-called structural formulæ. The first is of actual material significance, it is founded on the observation that the atoms may have their capacity of combination satisfied by a certain number of equivalents of other atoms or radicals, no matter what the nature of these atoms or radicals may be. The representation of this fact by structural formulæ, in the first instance at least, is purely formal; it only serves to aid the mind in comprehending and retaining the relations experimentally found, and shows whether the postulates of the theory of valency are fulfilled.

The valency of hydrogen is usually taken as unity, because according to all our experience a single atom of any element can only

unite with one definite number of hydrogen atoms, the law of multiple proportions finding no application to the hydrogen compounds that contain only one atom of the other element. Unfortunately, only few elements form hydrogen compounds, so that our ability to fix the valency in this way is limited. We have, nevertheless, arrived at a knowledge of the valency of elements that form no hydrogen compounds, by means of elements or radicals that have been directly found to be univalent with respect to hydrogen.\* Considerable difficulties have, however, been encountered here, and these are even yet not entirely overcome.

The most remarkable relation of the valencies, as far as they are known, is to be found in the periodic system, for they too form a periodic function of the atomic weight. The valency in the table (which is here reproduced) is constant in the horizontal rows, and increases by a unit from row to row as we descend. From the fifth row downwards it decreases just as regularly if we take the hydrogen compounds as decisive; the chlorine and oxygen compounds, on the other hand, still show the regular increase.

			1	2	3	4	5	6
I	R <sub>2</sub> O		Li	K	Rb	Cs	—	—
II	R <sub>2</sub> O <sub>2</sub>		Be	Ca	Sr	Ba	—	—
III	R <sub>2</sub> O <sub>3</sub>		B	Sc	Y	La	Yb	—
IV	R <sub>2</sub> O <sub>4</sub>	H <sub>4</sub> C	C	Ti	Zr	Ce	—	Th
V	R <sub>2</sub> O <sub>5</sub>	H <sub>3</sub> N	N	V	Nb	Di	Ta	—
VI	R <sub>2</sub> O <sub>6</sub>	H <sub>2</sub> O	O	Cr	Mo	—	W	U
VII	R <sub>2</sub> O <sub>7</sub>	HF	F	Mn	—	—	—	—
VIII			<div style="display: flex; align-items: center; justify-content: center;"> <div style="margin-right: 10px;"> <math>\left\{ \begin{array}{l} \text{Fe} \\ \text{Co} \\ \text{Ni} \end{array} \right.</math> </div> <div style="margin-right: 10px;"> <math>\left\{ \begin{array}{l} \text{Ru} \\ \text{Rh} \\ \text{Pd} \end{array} \right.</math> </div> <div> <math>\left\{ \begin{array}{l} \text{Os} \\ \text{Ir} \\ \text{Pt} \end{array} \right.</math> </div> </div>					
I	R <sub>2</sub> O		Na	Cu	Ag	—	Au	—
II	R <sub>2</sub> O <sub>2</sub>		Mg	Zn	Cd	—	Hg	—
III	R <sub>2</sub> O <sub>3</sub>		Al	Ga	In	—	Tl	—
IV	R <sub>2</sub> O <sub>4</sub>	H <sub>4</sub> Si	Si	Ge	Sn	—	Pb	—
V	R <sub>2</sub> O <sub>5</sub>	H <sub>3</sub> P	P	As	Sb	—	Bi	—
VI	R <sub>2</sub> O <sub>6</sub>	H <sub>2</sub> S	S	Se	Te	—	—	—
VII	R <sub>2</sub> O <sub>7</sub>	HCl	Cl	Br	I	—	—	—

Here again we see how some elements belong to different rows. As already mentioned, Mendelejeff was the first to call attention to these relations.

Notwithstanding the agreement of numerous facts with the theory of valency, several important difficulties, particularly in organic chemistry, have stood in the way of its being rigorously and consistently carried out. First of all, the primary principle that the combining-tendency of atoms is always satisfied by the same number of equivalents is not general. There are many compounds which for a certain quantity of one element have

\* The reader who wishes a detailed account of this subject is referred to Lothar Meyer's *Modern Theories of Chemistry*, English translation.

different numbers of equivalents of other elements, as, for example, carbon monoxide, CO, and carbon dioxide, CO<sub>2</sub>; nitrogen monoxide, N<sub>2</sub>O, nitrogen dioxide, NO, and nitrogen peroxide, NO<sub>2</sub>. Stress must be laid on the fact that these are all bodies whose vapour densities are known, so that there can be no doubt as to their molecular weights.

Two explanations of this have been offered. The hypothesis of constant valency was by some asserted to be strictly true, and the compounds of an element were called unsaturated when all the valencies attributed to it from a consideration of the majority of its known compounds were not satisfied, the assumption being that in certain circumstances there could be compounds in which some of the valencies remained passive. The reason was not given why this should occur in certain cases only, and why the atoms did not assume the arrangement—always theoretically possible—in which all the valencies would be satisfied, nor was the question disposed of why the atoms should have a definite valency at all.

Other chemists assumed that the valency could change, that in nitric oxide, NO, for example, the nitrogen as well as the oxygen was bivalent. This way of representing the facts is no more an explanation of them than the assumption of unsaturated valencies. Nevertheless, the strife between the supporters of constant and variable valency has been sufficiently bitter, and is even yet not at an end.

If we think of the way in which a decision might be arrived at, we see that it can only come from a definite and well-founded hypothesis as to the nature of what we call valency. As long as we denote by it merely the combining-capacity expressed in equivalents, we must grant that it has sometimes been found to change, and must therefore assume a variable valency. On the other hand, if we consider valency, as is mostly done, to be an inherent property of the atoms, the assumption that it is variable seems impossible, as we cannot admit any variation in the properties of atoms, but only a variation in their condition.

There still remains, however, one possibility of explaining the actual changes in the valency. If we conceive valency as a consequence of a property of the atoms, its action being modified by differences in their condition, especially by differences in their states of motion, it is comprehensible that although the cause of valency is invariable, the action of this cause, the valency itself, may appear different from case to case.

A hypothesis of this kind was advanced by van't Hoff (1878). By assuming that the chemical attraction between two molecules is caused by gravitation, he showed that if an atom possessed a form other than spherical, the intensity of the attraction at its surface would have a certain number of maxima dependent on the form. If the thermal motion of the atom were brisk, only the strongest maxima would be able to retain their atoms, and the valency would thus appear, as is actually the case, smaller at high than at low temperatures.

This assumption possesses all the qualifications of a hypothesis capable of development. It postulates no special properties, but is based on what pertains to the atoms as finite quantities of matter, namely form. The future must decide if it can be carried out fully, and if there may be drawn from it deductive laws whose experimental verification will prove its utility.

The need of finding an explanation for a great class of compounds, mostly known only in the solid state, and whose constitution cannot be explained by the ordinary assumptions as to the valency of the atoms, has led the supporters of constant valency to consider these compounds as being of a different order from those which come under the ordinary rules of valency. These bodies are called molecular compounds in contradistinction to the usual or atomic compounds. The former, which are made to include salts with water of crystallisation, double salts, and (by some) all the salts of ammonia, are not supposed to owe their chemical coherence to the forces acting between atom and atom that condition the valency; but the molecules from which these compounds originate are assumed to exert as wholes such forces on each other as serve to keep the compound together.

The molecular compounds have been only distinguished from the atomic compounds on account of the hypothesis of constant valency—a fact which inclines one to look upon this hypothesis with suspicion, especially as all exertions to find a distinction between the two classes other than that with respect to the valency have proved fruitless. For the rest, the properties of the one class pass gradually into those of the other, a continuous descent from greatest to least stability appearing with corresponding compounds.

The fundamental assumption too with regard to the nature of the distinction between atomic and molecular compounds is untenable. So long as we make none as to the nature of “valency,” the distinction in question is completely nugatory. On the other hand, if the valencies are conceived as localised maxima of attraction in the atom, we can only suppose that when molecules attract each other as wholes these maxima are active in some of the atoms in the molecules, so that the so-called attraction of the entire molecules is again reduced to the attractions between the atoms. That compounds of this kind, held together by the weaker secondary valencies, are more easily decomposable than the so-called atomic compounds is what we might expect, and involves no contradiction.

The foregoing considerations show how far the doctrine of valency is from deserving the name of a theory of chemical compounds. It has inherited from the parent theory of types so much of the merely formal element, that the attempt to make the actual relations clear by means of a mechanical hypothesis has scarcely been undertaken. At the present time chemists are mostly satisfied with the fact that structural formulæ provide schemes which represent the actual cases of isomerism and the possible reactions.

It is not intended by this to pronounce an unfavourable opinion with regard to the importance of structural formulæ. These stand much in the same relation to the substances they represent as the formulæ of analytical geometry to the corresponding curves and surfaces, only they do not approach the latter in respect of certainty

and completeness of representation,—a difference lying in the nature of the two branches of science. They afford to the expert the means of drawing a great number of conclusions, and of expressing a large number of facts in a concise and intelligible manner.

They are misused when they are taken as representing the actual arrangement of the atoms in space. The ordinary arrangement of the four valencies of a carbon atom in one plane evidently cannot correspond to the facts, for according to it there ought to be two methylene

chlorides, say,  $\begin{array}{c} \text{Cl} \\ | \\ \text{H}-\text{C}-\text{H} \\ | \\ \text{Cl} \end{array}$  and  $\begin{array}{c} \text{Cl} \\ | \\ \text{H}-\text{C}-\text{Cl} \\ | \\ \text{H} \end{array}$ , whereas only one is known,

and nothing points to the possibility of such isomers. We make this customary method of formulation conformable to the facts by explaining that the two formulæ given above are identical, which of course they in reality are not.

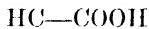
Van't Hoff, the first to indicate a mechanical theory of valency, was also the first to essay a tridimensional formulation of the atomic space-relations (1877). He imagines the valencies of the carbon atom to act at the four summits of a tetrahedron. On this assumption, only one methylene chloride is possible, and attention has been already called to the circumstance that the phenomena and conditions of optical activity are in satisfactory agreement with it.

Quite recently (1887) Johannes Wislicenus has further developed this idea by taking into consideration the forces acting between the different atoms, so that an intelligible explanation has been given of many phenomena not hitherto understood. The existence of more isomers among the unsaturated compounds than the ordinary structural formulæ indicate is clearly explained by the tridimensional diagrams, and in the same way also, the transformations of these substances into one another.

For example, there is only one structural formula to represent both

$$\text{HC}-\text{COOH}$$

fumaric and maleic acids, viz.  $\parallel$  . Van't Hoff had already shown



that two tridimensional formulæ correspond to this plane formula, if we imagine the valencies of the carbon atoms at the summits of a tetrahedron, viz.—

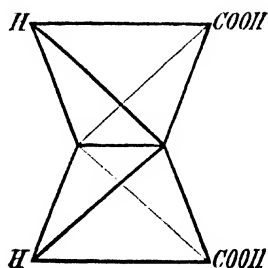


FIG. 43. MALEIC ACID.

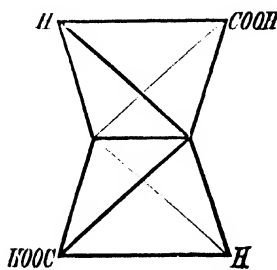


FIG. 44. FUMARIC ACID.

The first formula belongs to maleic acid, for this acid can form an anhydride, which according to the second formula is scarcely possible on account of the distance between the carboxyl groups.

Now, maleic acid under the influence of hydrobromic acid changes into fumaric acid. The process may be so represented that the elements of hydrobromic acid are added to maleic acid, thus forming monobromosuccinic acid, and are then again split off as hydrobromic acid. Meanwhile the carbon tetrahedra have become free to turn on their common axis, so that they will assume the position which best satisfies the affinities at work, whereupon the separation of hydrobromic acid takes place.

First, therefore, we have

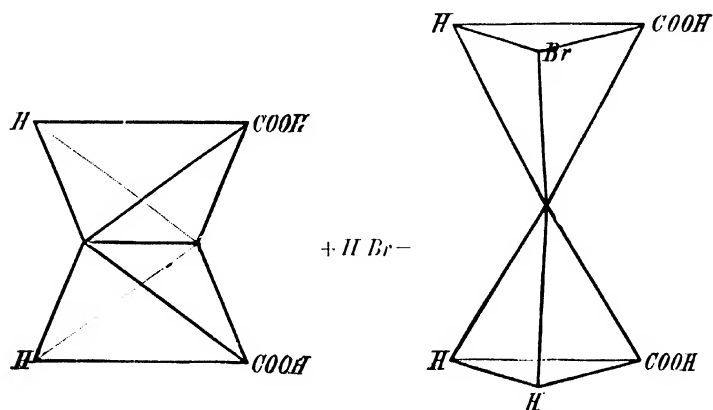


FIG. 45. MALEIC ACID.

FIG. 46. MONOBROMOSUCCINIC ACID.

The monobromosuccinic acid now undergoes a change on account of the mutual repulsion of the hydrogen atoms, whereby the positive and negative

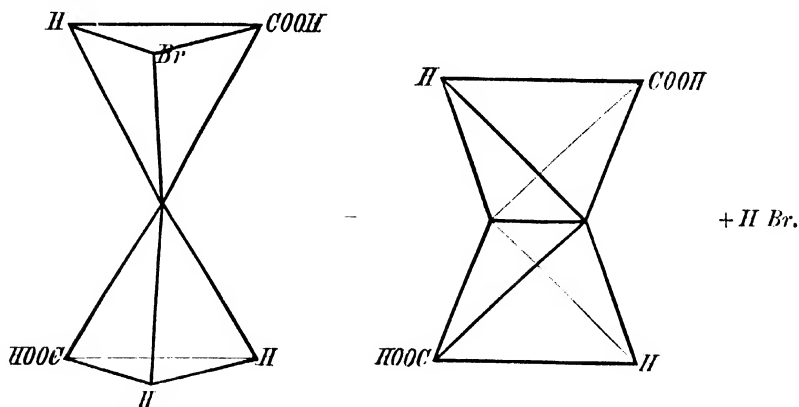


FIG. 47. MONOBROMOSUCCINIC ACID.

FIG. 48. FUMARIC ACID.

groups come opposite each other. If now hydrobromic acid separates from this, fumaric acid alone can be formed.

Corresponding to this example, other hitherto incomprehensible phenomena can be easily explained, as may be seen in the published work of Wislicenus and his pupils.

In these geometrical considerations we see a necessary and therefore well-justified stage of development of the theory of chemical structure on the basis of the doctrine of valency. The ideas, it is true, are of a purely hypothetical character; in this, however, they do not differ from the generally accepted atomic and molecular theories themselves. Every hypothesis must be specialised as far as the facts require. As soon as the formulæ written without respect to the geometrical relations became incapable of representing all the observed phenomena, an extension of their signification was rendered necessary, and this was made by taking the geometrical relations into account. The chief object of such hypothetical generalisations—that of simplifying the representation and of inciting to fresh research—has in the case of the geometrical formulæ already been fully attained. Not only have old facts been made clear through it for the first time, but a considerable number of new substances have been searched for at its instance—searched for and in almost all cases found.

## PART II

### CHEMICAL LAWS OF ENERGY





# BOOK VII

## THERMOCHEMISTRY

### CHAPTER I

#### INTRODUCTORY

BESIDES matter, the quantity of which undergoes no change in any known process, there is another something possessing the same properties of indestructibility and uncreatability, and having therefore a real existence in the same sense as this is ascribed to matter. This thing we call energy. It can appear in various forms—as the kinetic energy, or *vis viva*, of moving masses, as the potential energy (or capacity of doing work) of such material systems as are capable under the prevailing conditions of assuming a more stable arrangement, as heat (including light), as electrical energy, with which magnetic energy is to be associated, and, finally, as chemical energy.

All these different forms can be so transformed into each other that definite quantities of any one correspond to definite quantities of the others. Whenever energy in any form disappears, a proportionate quantity of another form must appear in its place; and to obtain a quantity of energy in any form we must sacrifice a proportionate quantity of some other kind of energy.

In our previous consideration of chemical processes the transformations were only looked at with respect to their material result; the causes necessary for a transformation to take place at all were not alluded to. These causes will now form the subject of our further investigation.

In general they are to be found in the circumstances and relations of energy. Energy is always associated with matter, at least we know no matter without energy, and every state of the former is defined by the amount of the definite kinds of energy it contains.

Now, energy is of such a nature that it is not possible for any masses affected with any kind of energy to exist together. Certain definite conditions must be complied with in order that this coexistence may be possible, and if these are not at first fulfilled an interaction takes place, with the result that they finally are fulfilled. In this property of energy lies the cause of all change in the material world.

Energy may in general be decomposed into two factors. Kinetic energy, for example, has the form  $m \frac{v^2}{2}$  where  $m$  is the mass and  $v$  the velocity of the moving body. Potential energy appears in the form  $fs$ ,  $s$  being the space passed over by the point considered in the change of state, and  $f$  the measure of the striving of the point to alter its state; this magnitude  $f$  is usually termed force.

For heat we have the product  $ts$ , where  $t$  is the temperature and  $s$  the specific heat; electrical energy is of the form  $eq$ ,  $q$  representing a quantity of electricity, and  $e$  the electromotive-force. No decomposition into two factors has as yet been made with chemical energy; possibly it may have the form of kinetic energy, as it is proportional to the mass.

The law of energy above-mentioned, which must be fulfilled in order that substances may exist together, is as follows:—One of the factors of the energy, which we may call the **intensity** of the energy, must have the same value in all parts of the system. This factor is—

for kinetic energy . . . .	velocity,
„ potential energy . . . .	force,
„ heat . . . . .	temperature,
„ electrical energy . . . .	electromotive-force.

Whenever one of these magnitudes has different values at different parts of the system, the latter cannot remain at rest, and the appropriate process takes place.

In many cases one intensity can be partially replaced by another, but we shall not enter on the difficult question as to the conditions of such a substitution.

When one intensity becomes adjusted, this mostly entails such a change of state that an inequality is brought about in some other intensity. Thus one change conditions another, and so it goes on. Still, so far as we can judge, this process cannot continue for ever; in some extraordinarily remote time to come the intensities will everywhere have assumed uniform values and all change will cease.

Chemical energy is to us the least known of all the various forms, as we can measure neither it nor any of its factors directly. The only means of obtaining information regarding it is to transform it into another species of energy. It passes most easily and completely into

heat, and the branch of science which treats of the measurement of chemical energy in thermal units is called thermochemistry. Thermochemistry is thus the science of the thermal processes conditioned by chemical processes. The quantities of heat evolved or absorbed measure the decrease or increase of chemical energy, in so far as other energy is not involved in the processes.

The sources of energy employed in the arts and manufactures are all of chemical origin, being referable to the combination of the elements of the fuel employed with the oxygen of the air. But, in addition to this, the vital activity of all organisms depends exclusively on chemical processes and the energy liberated through them. Chemical energy is consequently that form with which we have most extensively and frequently to deal, and which has the first and largest place in the economy of nature.

The history of thermochemistry begins accordingly with the technological and physiological problems propounded by Lavoisier and Laplace, Rumford, Dulong, Despretz, etc., who also attempted their solution. A theoretical foundation on one side is due to the first-named, who stated the principle that as much heat is required to decompose a compound as is liberated on its formation from the elements. This is a particular and very simple case of the general law of energy.

The law for thermochemical processes was first enounced in its full extent by G. H. Hess (1840) as the law of constant heat-summation. He stated that the initial and final stages alone determine the development of heat in chemical processes; if these are specified, the development of heat is given, whatever may be the intermediate stages.

According to our present notions a definite value of the energy of a system corresponds to each state it may assume, that which we call the "state" of the system being in fact ideally fixed by the nature and quantity of the energy associated with the matter in the system. Two states therefore correspond to two quantities of energy, the difference of which must be conducted to or from the system if it shall pass from one state to the other. In how many portions this energy may be communicated has evidently no effect on the final value.

Hess established his principle as a conclusion from experiment, with full consciousness, however, of its wide import. He tested it in various ways, and from his numbers the following table is selected :—

			Sum.
$\text{H}_2\text{SO}_4$	—	+ $2\text{NH}_3$ (in solution)	595.8
$\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$	77.8	"	518.9
$\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$	116.7	"	480.5
$\text{H}_2\text{SO}_4 + 5\text{H}_2\text{O}$	155.6	"	446.5
		P	601.8

The first column of figures represents the quantities of heat liberated by the action of one molecule of sulphuric acid on one, two, and five molecules of water; the second represents the quantities of heat evolved on the neutralisation of the acids so diluted with ammonia. The sum of the corresponding members of both is approximately constant.

The significance of this principle for the practice of thermochemistry is very great. It enables us to calculate the heat effect of processes which cannot be directly measured; for we may represent them as terms of a sum, of which the total value and the other terms are known. We cannot, for example, measure the heat given out on the combustion of carbon to carbon monoxide. If, however, we measure the heat evolved when carbon is oxidised to carbon dioxide, then this must be equal to the heat of combustion of carbon to monoxide plus that of monoxide to dioxide. The latter can also be directly ascertained, so that the difference of the two observed values gives the required heat of combustion of carbon to carbon monoxide.

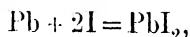
Contemporaneously with Hess, who is to be looked upon as the real founder of thermochemistry, and after him, other investigators were busy at this subject, viz. Andrews, Graham, and especially Favre and Silbermann, who collected a rich store of observations. In clearness of ideas, however, these are all inferior to Hess.

The results of the mechanical theory of heat, which had meantime been developed, were first applied to thermochemistry by Julius Thomsen (1853.) This chemist has up to the present time continued his thermochemical work, and has accumulated an enormous number of data, mostly determined with considerable accuracy. Berthelot in 1865 began to occupy himself with similar problems. It is to these two investigators that we owe the greatest part of our acquaintance with the domain of thermochemistry.

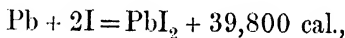
## CHAPTER II

### THERMOCHEMICAL METHODS

IN order to formulate the facts of thermochemistry shortly and in a form suitable for calculation, we shall extend the signification of the ordinary chemical equations in such a way that they will represent not only the mass-relations but also the energy-relations. For example, when we write the equation

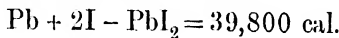


this states that lead iodide is formed from lead and iodine, 206.9 g. lead and 253.8 g. iodine giving 460.7 g. lead iodide. If the formulæ are to represent, not the quantities of the substances, but the quantities of energy associated with them, the equation is incomplete. For on the formation of lead iodide heat is liberated to the amount of 39,800 cal.; the energy of lead iodide is less than the energy of its components by this quantity. The corresponding equation for energy is therefore

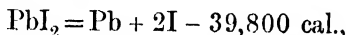


and signifies that 206.9 g. lead and 253.8 g. iodine together contain as much energy as 460.7 g. lead iodide plus 39,800 cal.

The equation may be algebraically transformed, but then its signification is somewhat different. Thus



means that the difference of energy between lead plus iodine, and lead iodide amounts to 39,800 cal. Or

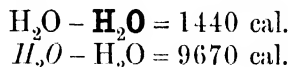


represents that when lead iodide is decomposed into lead and iodine, 39,800 cal. must be supplied.

The equations are all to be so understood that the energy of the substances only holds for one and the same temperature, usually the mean laboratory temperature of 18°.

The amount of energy in a substance is further dependent on its state of aggregation. It is simplest to indicate the state by the type

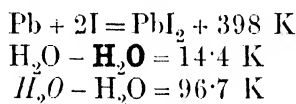
employed. Ordinary type will be taken to represent liquids, which are most frequently under consideration. Gases will be indicated by italics; solids by thick type. Then the equations



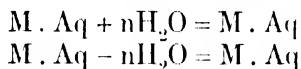
signify that on the transformation of water into ice 1440 cal. are liberated, and on the transformation of water vapour into liquid water, 9670 cal.

It may be observed, as we have till now tacitly assumed, that the quantities of energy and heat refer to such quantities of the substances as amount to their formula-weights in grams.

The small calorie hitherto used is too small for the roughness of thermochemical measurements, so that we shall employ in the sequel a unit one hundred times greater, which we may denote by K. It is that quantity of heat which a gram of water loses when cooled from  $100^\circ$  to  $0^\circ$ . The above equations now become

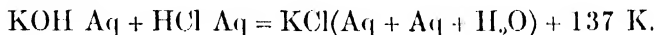


The reacting substances are very often dissolved in a large quantity of water. This is denoted by adding the letters Aq (aqua) to the ordinary chemical symbol. Such solutions when further diluted with water neither absorb nor evolve heat. Thus the equations

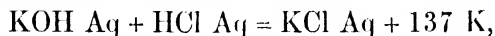


hold good, M being the dissolved substance. We may therefore in thermochemical equations add or subtract limited quantities of water when the substances are in solution without committing any appreciable error.

For instance, we have for the formation of potassium chloride in aqueous solution—

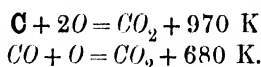


Instead of this equation we always write

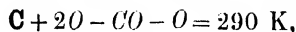


as the mixing of the liberated water with the solution of potassium chloride has no thermal effect whatever.

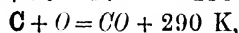
These energy-equations are specially useful in calculating thermochemical data which cannot be directly observed. If we return to the example given by Hess (p. 210), we have from direct measurement



Subtracting the lower from the upper equation we get

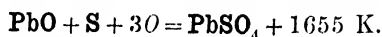


or

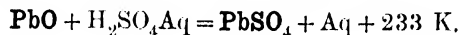


*i.e.* the heat of combination of carbon and oxygen to form carbon monoxide is 290 K.

A second somewhat more complicated example is the heat of formation of sulphur trioxide, also determined by Hess. The process consisted in burning a mixture of lead oxide and sulphur in oxygen. Lead sulphate is formed with an evolution of 1655 K; we have therefore the equation



To eliminate the terms PbO and PbSO<sub>4</sub>, lead oxide was transformed into lead sulphate by solution in sulphuric acid; the result was—



Subtracting, we get



*i.e.* the formation of aqueous sulphuric acid from sulphur, oxygen, and water is accompanied by the evolution of 1422 K.

Lastly, Hess dissolved sulphur trioxide in water—

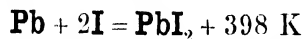


Subtracting again, we have as the final and desired result —



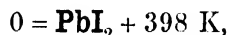
In the same way a great many other problems may be solved. The method is to measure any two reactions in which the initial and final substances take part, and then to eliminate the subsidiary bodies by suitable equations between them. It depends upon the skill of the experimenter so to choose the reactions that the measurements may be as exact as possible, and that the end may be attained with the fewest possible intermediate stages.

The heat of formation is a heat of reaction extremely often measured. By this name we indicate the difference between the energy of a chemical compound and that of its component elements. The numbers are obtained from equations in which only the elements and the compound occur. It follows from

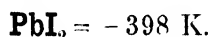


that the heat of formation of lead iodide is 398 K.

This heat is therefore the loss of energy suffered by the elements when they unite to form the compound in question. If the quantities of energy, whose absolute magnitudes are quite unknown, be reckoned from the energy of the elements taken as zero, the equation assumes the form



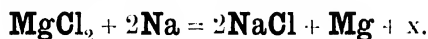
if we make Pb = 0 and 2I = 0. This can also be written





Therefore in the energy-equations the formulæ of the compounds may be replaced by their heats of formation with the signs changed.

In this way we can easily calculate heats of reaction by means of the heats of formation. Suppose we wish to find the heat given out in the preparation of magnesium. We have



Now the heat of formation of magnesium chloride is 1510 K, and of sodium chloride 1954 K. Making the substitution and putting the heats of formation of the elements equal to zero, we obtain

$$\begin{aligned} -1510 + 2 \times 0 &= -2 \times 1954 + 0 + x \\ x &= 2398 \text{ K.} \end{aligned}$$

On account of this simple form taken by the equations, it is usual to determine the heat of formation of the various chemical compounds, so that the values may be used in further calculations. Heats of formation are consequently given by preference in the tables contained in the following chapters.

With respect now to the actual performance of thermochemical experiments, there are several general statements that may be made, in spite of the variety in the methods and apparatus employed by different investigators. Only a relatively small number of the numerous reactions known to experimental chemistry are suitable for thermochemical measurement; these being almost exclusively such as take place at ordinary temperatures and are at an end in the space of a few minutes. The chief among them are the phenomena of neutralisation, of solution, and of dilution.

A second class of thermochemical processes is formed by rapid combustions, which, by being conducted in a completely closed vessel surrounded by water, are likewise amenable to convenient measurement. The majority of thermochemical experiments may be reduced to one or other of these forms.

For thermochemical measurements in aqueous solution calorimeters constructed of glass or metal (platinum by preference) are used.

If the dissolving of a solid, liquid, or gas in the liquid of the calorimeter is in question, the experiment is so conducted that the substance is brought as nearly as possible to the temperature of the calorimeter and the process then initiated. The uniform distribution of the heat as well as of the reacting substances is provided for by an efficient stirring apparatus. This has usually the form of a horizontal plate, which contains suitable openings for the passage of a thermometer, etc., and has an up and down motion. It is better, however, to give the stirrer the form of a screw-propeller, and have it near the bottom of the calorimeter, the motion in this case being of course one of rotation. By this arrangement we avoid wet portions of the apparatus being exposed to the air and getting cooled by evaporation. The mechanical action too is much easier, and the space inside the calorimeter is left freer.

If the reaction is to be between two approximately equal quantities of

liquid, the temperature of each must be accurately measured at the moment of mixing. Thomsen in this case arranges a smaller vessel on the top of his calorimeter, each vessel being provided with thermometer and stirrer, and after having read off the temperature of both, lets the liquid in the upper vessel flow through a valve in the bottom into the lower vessel. Berthelot introduces one of the liquids into his calorimeter, but then, unlike Thomsen, has the other in a thin-walled, wide-necked flask standing inside a protective copper cylinder with a silvered and polished interior. When the temperature has been ascertained, the thermometer serving as stirrer, the flask is seized by means of wooden tongs and its contents emptied into the calorimeter. He rejects Thomsen's arrangement because the liquid in flowing through the valve may possibly experience a change of temperature. This objection is unfounded, however, for by the way in which Thomsen makes his thermometers comparable, an error of this nature is eliminated. In reality, Thomsen's apparatus is the more exact, which is most likely owing to the fact that his thermometers are read off through a telescope, while Berthelot uses the naked eye.

The calorimeter employed for the combustion of solid, liquid, and gaseous substances in gases has been gradually evolved from the imperfect instruments of Dalton, Davy, and Rumford, by the labours of Dulong, Despretz, and in particular of Favre and Silbermann. It consists of a cylinder filled with water into which the combustion-chamber is sunk; a number of tubes, destined to supply the necessary gases, open into it, and the products of combustion are led through a long spiral metal tube or worm, in order that all their excess of heat may be given up to the water of the calorimeter.

The apparatus has experienced but little change in the course of time. Thomsen makes the metallic parts of platinum, and Berthelot has introduced a glass combustion-chamber, which admits of very convenient observation of the progress of the reaction.

Besides the gradual combustion in an atmosphere of gas, several other methods of combustion have of late been practised. There is, for example, the explosive combustion, a suitable gaseous mixture being enclosed in an apparatus immersed in the water of the calorimeter, and fired by means of the electric spark. Andrews seems first to have availed himself of this method in a special case, and Berthelot has extended its application greatly by using what he calls a "calorimetric bomb." This apparatus consists of a hollow metal sphere in which the gas is compressed, and exploded after the whole has been immersed in the calorimeter.

Another process is the combustion with combined oxygen (especially with potassium chlorate), first employed by Frankland (1866), and later improved and applied by Stohmann and his pupils. The substance is here mixed with potassium chlorate and some indifferent material (*e.g.* pumice), and made into a sort of firework, which is set off inside a water-calorimeter. The details cannot be given here. It has this advantage, that substances can be investigated by its means, to which the other methods, on account of irregular or imperfect combustion, are not applicable. The drawback of the

method is that the combustion often miscarries, and that the numbers obtained are affected by numerous and considerable corrections.

It should be mentioned, in conclusion, that Bunsen's ice-calorimeter has been in some cases used for thermochemical experiments. Although this method gives very exact results, even with small quantities of substance, it requires excessively skilful manipulation, and can only be applied in winter, as the instrument must be set up in a cold place, the temperature of experiment being  $0^{\circ}$ . Working at this temperature is frequently an advantage, but in certain cases decidedly detrimental.

The measurement of temperature is at once the most important and the most difficult part of a calorimetric determination. It is true that very sensitive thermometers can be constructed by the employment of narrow capillaries and somewhat large bulbs, and as a rule we use such as are divided into  $\frac{1}{500}$  degree, which therefore admit of the estimation of  $\frac{1}{500}$  degree when read off with a telescope. The difficulty, however, lies less in the want of sensibility in the thermometers than in the continual heat-exchange of the calorimeter with the surrounding objects, the proper thermal result being more or less disturbed by this. The error is greater with a small calorimeter, as the surface in such a case is larger with respect to the contents. This circumstance has been frequently neglected, and has often been the cause of great uncertainty. Berthelot in the course of his thermochemical work studied the subject with some care, and arrived at the conclusion that with a calorimeter of 500 c. cm. capacity we get the minimum error, the disturbance falling in this case within the limits of accuracy given by the measurement of temperature.

As the interchange of heat by radiation assumes greater proportions as the difference of temperature between the calorimeter and its environment is greater, we must attend to both having as nearly as possible the same temperature. It is besides desirable to perform all calorimetric experiments at a uniform temperature, else they are not strictly comparable, and the determination of the influence of temperature would considerably increase the work. Thomsen therefore uses a laboratory, the heating apparatus of which can be easily regulated, and always brings its temperature as near as may be to  $18^{\circ}$  before he commences his experiments. Berthelot, who, in other respects also, does not insist upon the last degree of accuracy, works within the tolerably wide limits of temperature of an ordinary laboratory.

To diminish the radiation as much as possible the calorimeter is brightly polished, and placed within a cylinder also polished in the interior. Berthelot surrounds this last with a large jacket of tin-plate filled with water; Thomsen prefers to employ cases of metal or cardboard, the intervening spaces merely containing air.

For the method, due to Regnault, of freeing the measurements of temperature from the effects of radiation, the larger text-books must be consulted. Rumford's artifice of having the temperature before the experiment as far on one side of the atmospheric temperature, as it will be on the other when the action is over, finds an application here, especially in the

employment of the combustion calorimeter. In fact, it was in his calorimetric determinations of the heating power of fuel that Rumford first employed this method.

The number of calories developed in a thermochemical reaction is obtained by multiplying the thermal capacity of the calorimeter by the (corrected) change of temperature. To get the result in the units given above (p. 212), this number has still to be multiplied by the ratio of the substance used to its formula-weight, both being expressed in grams.

With regard to the thermal capacity of the calorimeter, the water-equivalent of the vessel, the stirrer, the thermometer, and all the other parts of the apparatus that suffer the change of temperature must be determined or calculated in the usual way. If the liquid employed is not water, its specific heat must also be known. As the specific heat of a solution is not deducible from the specific heats of the dissolved substance and the solvent, special determinations would in almost all cases have to be made. Thermochemists have hitherto sought to elude the not inconsiderable complication here involved by making certain assumptions, which without a knowledge of the numbers in question may lead to very inaccurate calculations. Thomsen puts the thermal capacity of his solutions equal to that of the water contained in them. This assumption, tested in detail by Thomsen himself, is only very seldom quite accurate; the errors are sometimes positive, sometimes negative, but in all cases very small for dilute solutions, which are nearly always here in question.

An idea of the admissibility of such a proceeding may be obtained by calculating the difference between the thermal capacity of aqueous solutions and that of the water contained in them. It will be found that the difference usually does not amount to one per cent—only in extreme cases is it greater. The accuracy of calorimetric experiments varies a good deal, but it is often greater than this, so that it cannot be denied that the results are somewhat impaired by the above mode of calculation.

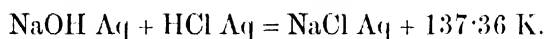
To find the observed thermal effect we have the formula

$$Q = (t_c - t_a)a + (t_c - t_b)(b + p),$$

where  $t_a$  is the temperature of the substance outside the calorimeter proper,  $t_b$  of that within the calorimeter, and  $t_c$  the corrected final temperature after the reaction;  $a$  is the calorimetric equivalent of the first substance,  $b$  that of the second (*i.e.* in the mixture-calorimeter the quantities of water in the solutions employed). Lastly,  $p$  is the water-equivalent of the calorimeter.

Thus, for example, the heat of neutralisation of hydrochloric acid with soda was found by Thomsen to be 13,736 cal., by mixing  $\frac{1}{8}$  formula-weight or  $\frac{1}{4}$  equivalent of each of two solutions having the composition  $\text{Na}_2\text{O} + 200\text{H}_2\text{O}$  and  $\text{H}_2\text{Cl}_2 + 200\text{H}_2\text{O}$ , with one another. The solution in the calorimeter had a temperature of  $18^\circ.610$ ; the

solution in the upper vessel was at  $18^{\circ}\cdot222$  ; after mixing the corrected temperature was  $22^{\circ}\cdot169$ . The solutions had consequently experienced a rise of temperature of  $3^{\circ}\cdot559$  and  $3^{\circ}\cdot947$  respectively. Multiplying these by the weight of water, 450 g. ( $=\frac{1}{8} \times 200\text{H}_2\text{O}$ ), 13 g. being added to the first solution as the water-equivalent of the calorimeter, we obtain  $1648 + 1786 = 3434$  cal., so that multiplying this value by 4, as only  $\frac{1}{4}$  equivalent was used, we get 13,736 cal. as the heat of neutralisation of one equivalent of soda by one equivalent of hydrochloric acid, or



Berthelot diverges from Thomsen's method, inasmuch as he does not determine the thermal capacity of his solutions according to the weight of water, but according to the total volume. He consequently does not use solutions of the composition indicated by certain ratios of the formula-weights, but such as are employed in volumetric analysis, a formula-weight of the substance being contained in a litre, or in a multiple or sub-multiple of a litre. Berthelot shows that the approximation to the truth obtained by this mode of reckoning is in some cases greater than that got from the method practised by Thomsen ; in other cases, however, it is just the reverse. On the whole, we may say that Berthelot's method is more convenient in practice, but Thomsen's more precise in the definitions.

## CHAPTER III

### SALT-FORMATION

IN spite of recent researches throughout the whole domain of chemistry with respect to the heat developed in a reaction, very few general relations have been established. The most general had already been found by Hess, and formulated by him as the Law of Thermo-neutrality. It states that on the double-decomposition of neutral salts in solution, heat is neither evolved nor absorbed.

This rule is not absolutely correct, for small thermal changes always take place, and there are further some salts which do not obey the law at all. These, however, usually differ in most other respects also from the ordinary type of salts. It is assumed, too, that all the salts are in solution during the process and remain dissolved; when one of the salts separates in the solid form, the principle holds good no longer.

Hess assumed that the relation arose from the heat of neutralisation depending only on the acid. Andrews believed, on the other hand, that the base alone determined the evolution of heat. Both assumptions are wrong. Favre and Silbermann showed that different acids as well as different bases evolved different amounts of heat on neutralisation, but that the differences between the amounts of heat given out by any two bases with a series of acids, or of any two acids with a series of bases, had always the same value. If  $(a, b)$  denote the heat of neutralisation of the acid  $a$  with the base  $b$ , then in a table of the form

$$\begin{array}{llll} (a', b') & (a'', b') & (a''', b') & \dots \\ (a', b'') & (a'', b'') & (a''', b'') & \dots \\ (a', b''') & (a'', b''') & (a''', b''') & \dots \end{array}$$

the differences between corresponding pairs, whether taken horizontally or vertically, are equal, *i.e.*

$$\begin{array}{l} (a', b') - (a'', b') = (a', b'') - (a'', b'') = (a', b''') - (a'', b''') \dots \\ \text{and} \quad (a', b') - (a', b'') = (a'', b') - (a'', b'') = (a''', b') - (a''', b'') \dots \end{array}$$

This law corresponds perfectly to that which we found as a first approximation in the case of the molecular volumes of salt-solutions

(p. 143), and leads to the same conclusion. The heat developed on neutralising an acid with a base is additively composed of two terms, one of which depends only on the nature of the acid, and the other only on the nature of the base. We cannot at present determine the magnitude of these terms separately.

The various acids behave differently, although the differences are not great, when they are neutralised by one and the same base, say soda. The strong monobasic acids, like hydrochloric, hydrobromic, hydriodic, nitric, chloric, bromic, iodic, and perchloric acids, and besides these, alkyl-sulphuric and the sulphonic acids of organic chemistry, all behave surprisingly alike. On neutralisation of one equivalent by soda, a quantity of heat varying between 137 K and 141 K is evolved in each case. Excess of acid or soda has no effect. This circumstance indicates that the process taking place when these substances are neutralised is of substantially the same nature for all these different compounds.

The weak monobasic acids, of which the members of the fatty series especially have been investigated, differ somewhat from the stronger acids, their heat of neutralisation sometimes exceeding, sometimes falling below the numbers given above ; *e.g.*

Formic acid	134 K	Acetic acid	133 K
Acetic „	133 „	Monochloracetic acid	143 „
Propionic „	134 „	Dichloracetic „	148 „
Butyric „	137 „	Trichloracetic „	139 „
Valerianic „	140 „		

Here also, however, the differences are not very great.

Hydrofluoric acid is quite abnormal in this respect. In the first place, it has a very large heat of neutralisation, 163 K. Then an excess of the acid acts on the neutral salt, with the accompaniment of a slight absorption of heat (– 3 K), a fact standing in connection with the capability of hydrofluoric acid to form acid salts. The heat of neutralisation of hypophosphorous acid,  $\text{HPO}_2\text{H}_2$ , viz. 152 K, is also abnormal ; for the rest it behaves decidedly as a monobasic acid, a conclusion already arrived at from its purely chemical investigation.

Very weak acids, like hypochlorous and hydrocyanic acids, give very small heats of neutralisation, 98 K and 28 K respectively. This comes from their inability to neutralise soda completely in aqueous solution, which may be seen in the alkaline reaction of the salts, and in an excess of alkali by the action of mass producing a further amount of heat.

Amongst the dibasic acids there are several of exactly the same order as the strong monobasic acids. For each equivalent they give a heat of neutralisation of about 135 K, and an excess of acid has no action on the neutral salt. Such are chloroplatinic acid,  $\text{H}_2\text{PtCl}_6$ ,

dithionic acid,  $\text{H}_2\text{S}_2\text{O}_6$ , and in some degree hydrofluosilicic acid,  $\text{H}_2\text{SiF}_6$ .

Other dibasic acids, on the contrary, *e.g.* sulphuric acid, exhibit a totally different behaviour. If increasing quantities of sulphuric acid are added to one equivalent of soda, an evolution of heat takes place until the composition of the neutral salt is reached; it amounts to 157 K for one equivalent or 314 K for a gram-molecular-weight of sulphuric acid. If sulphuric acid be still added, an absorption of heat begins, which increases slowly with the amount of acid added, and appears to approach asymptotically to a limiting value of about - 33 K.

This peculiar conduct is usually explained by assuming that some acid sulphate,  $\text{NaHSO}_4$ , is formed in the solution, its formation being accompanied by a less evolution of heat than that required to separate the sulphuric acid from the water. We have here one of the interesting cases where a chemical reaction spontaneously takes place with absorption of heat.

Selenic acid is similar to sulphuric acid in this respect. Of the other dibasic acids, oxalic and tartaric acids are also to be mentioned as forming acid salts in solution with absorption of heat, although the absorption is very slight. Malic acid shows no action.

When an excess of succinic acid is added to a dilute solution of sodium succinate, a slight evolution of heat is observed. To this second group of dibasic acids having acid salts formed with evolution of heat there belong further sulphurous, selenious, and phosphorous acids. Carbonic acid and sulphhydric acid are so weak that their salts have an alkaline reaction, and cannot be formed completely from acid and base in aqueous solution. Boracic, arsenious, and silicic acids belong also to this class.

The tribasic acids act quite similarly to the dibasic acids.

What has been said above, strictly speaking, holds good only when soda is used to neutralise the acids, but in consequence of the law of thermoneutrality the foregoing relations are repeated with but little change when other bases are employed.

The alkalies and alkaline earths form a group of bases which have much the same character as the strong monobasic acids. In this group we also find thallium hydroxide, some of the platinamine and cobaltamine bases, and the organic ammonium and sulphonium bases. They have all the same heat of neutralisation with any one acid. Thus, when neutralised with hydrochloric acid, they give out from 136 to 140 K, and with sulphuric acid proportionately more. Ammonia and its organic derivatives among soluble bases have in part a considerably smaller heat of neutralisation, *e.g.* for hydrochloric acid—

Ammonia	122 K	Hydroxylamine	93 K
Methylamine	131 „	Aniline	75 „
Dimethylamine	118 „	o-Toluidine	76 „
Trimethylamine	88 „		



The bases of the magnesia series have also for the most part smaller heats of neutralisation. As they are all insoluble in water it might be believed that their heat of neutralisation is diminished by the heat of solution of the bases. This circumstance, however, does not seem to have a great effect, for in the case of magnesia itself the heat of neutralisation of the insoluble hydroxide is not very different from the values obtained for the soluble alkalis. The numbers determined by Thomsen for hydrochloric acid are—

	2 HCl		2 HCl
Magnesia	277 K	Ferrous oxide	214 K
Manganous oxide	230 „	Cadmium „	203 „
Nickelous „	226 „	Zinc „	199 „
Cobaltous „	211 „	Cupric „	149 „

The heats of neutralisation with sulphuric acid are regularly 35 to 36 K greater, as they ought to be according to Hess's law; most of the other monobasic acids give the same numbers as hydrochloric acid. The sesquioxides analogous to alumina behave differently from the above bases. Their heat of neutralisation is much smaller, and the differences between the values for hydrochloric and sulphuric acid are not equal. This arises from these bases being very weak; their salts decompose in solution to a greater or less extent into free acid and a basic salt, and thus their real heat of neutralisation is not observed at all.

## CHAPTER IV

### THERMOCHEMISTRY OF THE NON-METALS

IN accordance with the fact already stated that no general quantitative laws (with the exception of the law of thermoneutrality) are known in thermochemistry, little more can be given in the following pages than a collection of heats of formation. From these we can deduce by easy calculations the thermal changes accompanying the most diverse reactions (p. 214), so that the tables given represent very nearly all the known data of thermochemistry.\*

#### § 1. Oxygen.

Heat of Formation.

Ozone  $\text{O}_3$  - 300 K (approx).

The formation of ozone from ordinary oxygen is accompanied by considerable absorption of heat.

#### § 2. Hydrogen.

1. Water  $\text{H}_2\text{O}$  684 K liquid.

Latent heat of fusion - 14 K, heat of vaporisation at  $100^\circ$  - 96.7 K.

2. Hydrogen peroxide  $\text{H}_2\text{O}_2$  452 K

The heat of formation of the peroxide is less than that of water ; consequently the former passes into the latter and free oxygen, with an evolution of 232 K.

#### § 3. Chlorine.

1. Hydrogen chloride  $\text{HCl}$  220 K

Water absorbs the gas with evolution of 173 K.

2. Hypochlorous acid  $\text{Cl}_2\text{O}$  - 178 K  
 $\text{HClO, Aq}$  300 „

\* For all details the reader is referred to the author's *Lehrbuch der allgemeinen Chemie*, vol. ii.

Heat of Formation.

The heat of solution of the anhydride is 94 K.

3. Chloric acid	$\text{HClO}_3, \text{Aq}$	239 K
4. Perchloric acid	$\text{HClO}_4, \text{Aq}$	386 „

The anhydrous acid is dissolved in water with evolution of 203 K ; its heat of formation is therefore 183 K.

#### § 4. Bromine.

1. Bromine. The heat of fusion is  $-13$  K, and the heat of vaporisation at the boiling-point  $63^\circ$ ,  $-36$  K.

2. Hydrogen bromide	$\text{HBr}$	121 K
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The bromine is here supposed to be gaseous. For liquid bromine the heat of formation is 84 K. Water absorbs hydrogen bromide with evolution of 199 K.

3. Hypobromous acid	$\text{HBrO}, \text{Aq}$	335 K
4. Bromic acid	$\text{HBrO}_3, \text{Aq}$	160 „

In both cases the bromine is taken in the gaseous state.

#### § 5. Iodine.

1. Iodine. Heat of fusion,  $-15$  K ; heat of vaporisation,  $-30$  K. Boltzmann has calculated the heat of dissociation of  $\text{I}_2$  into  $2 \text{ I}$  and found it to be  $-285$  K.

2. Hydrogen iodide	$\text{HI}$	$-61$ K
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The formation of hydrogen iodide from hydrogen and solid iodine is accompanied by absorption of heat. Gaseous iodine would combine with hydrogen with almost no thermal effect. The gas dissolves in water with evolution of 192 K, so that the heat of formation of hydriodic acid,  $\text{HI}, \text{Aq}$ , is 131 K.

3. Iodic acid	$\text{HIO}_3$	582 K.
	$\text{HIO}_3, \text{Aq}$	560 „

The acid dissolves in water with absorption of 22 K. For the anhydride we have the heat of formation—

	$\text{I}_2\text{O}_5$	453 K.
4. Periodic acid	$\text{HIO}_4, \text{Aq}$	476 „

The heat of solution of the crystallised acid,  $\text{HIO}_4 \cdot 2\text{H}_2\text{O}$ , is only  $-14$  K.

5. Iodine monochloride	$\text{ICl}$	58 K	Heat of fusion $-23$ K
6. Iodine trichloride	$\text{ICl}_3$	215 „	
7. Iodine bromide	$\text{IBr}$	25 „	

#### § 6. Fluorine.

The heat of solution of hydrofluoric acid in water is 118 K.

### § 7. Sulphur.

1. Sulphur. Heat of fusion,  $-3$  K. The various modifications exhibit differences of energy of from 5 to 10 K.

		Heat of Formation.
2. Hydrogen sulphide	$\text{H}_2\text{S}$	27 K
The heat of solution in water is 46 K.		
3. Sulphurous acid	$\text{SO}_2$	710 „

This number is for the rhombic modification of sulphur and the ordinary temperature. The dioxide dissolves in water with evolution of 77 K, so that the heat of formation of the aqueous acid from hydrogen, oxygen, and sulphur is 1472 K.

4. Sulphuric acid	$\text{H}_2\text{SO}_4$	1931 K
	$\text{H}_2\text{SO}_4, \text{Aq}$	2109 „
	$\text{SO}_3$	1033 „
	$\text{SO}_3, \text{Aq}$	1425 „

The heat of solution of sulphuric acid in water is 178 K, that of the anhydride 392 K.

5. Hyposulphurous acid	$\text{H}_2\text{S}_2\text{O}_3, \text{Aq}$	1373 K
	$\text{S}_2\text{O}_2, \text{Aq}$	689 „
6. Dithionic acid	$\text{H}_2\text{S}_2\text{O}_6, \text{Aq}$	2796 „
	$\text{S}_2\text{O}_5, \text{Aq}$	2112 „
7. Tetrathionic acid	$\text{H}_2\text{S}_4\text{O}_6, \text{Aq}$	2612 „
	$\text{S}_4\text{O}_5, \text{Aq}$	1928 „
8. Sulphur monochloride	$\text{S}_2\text{Cl}_2$	143 „
9. Sulphur monobromide	$\text{S}_2\text{Br}_2$	10 „
10. Sulphuryl chloride	$\text{SO}_2\text{Cl}_2$	898 „
11. Thionyl chloride	$\text{SOCl}_2$	498 „
12. Pyrosulphuryl chloride	$\text{S}_2\text{O}_5\text{Cl}_2$	1630 „

### § 8. Selenium.

1. Hydrogen selenide	$\text{H}_2\text{Se}$	$-111$ „
2. Selenious acid	$\text{SeO}_2$	572 „
	$\text{SeO}_2, \text{Aq}$	562 „
	$\text{H}_2\text{SeO}_3, \text{Aq}$	1246 „
3. Selenic acid	$\text{SeO}_3, \text{Aq}$	768 „
	$\text{H}_2\text{SeO}_4, \text{Aq}$	1452 „
4. Selenium monochloride	$\text{Se}_2\text{Cl}_2$	222 „
5. Selenium tetrachloride	$\text{SeCl}_4$	462 „

### § 9. Tellurium.

		Heat of
1. Tellurous acid	$\text{TeO}_2, \text{Aq}$	773 „
	$\text{H}_2\text{TeO}_3, \text{Aq}$	1457 „
2. Telluric acid	$\text{TeO}_3, \text{Aq}$	985 „
	$\text{H}_2\text{TeO}_4, \text{Aq}$	1669 „

3. Tellurium tetra- chloride	$\text{TeCl}_4$	Heat of Formation. 774 K
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### § 10. Nitrogen.

1. Ammonia	$\text{NH}_3$	120 „	
	$\text{NH}_3, \text{Aq}$	204 „	
2. Nitrous oxide	$\text{N}_2\text{O}$	- 180 „	
3. Nitrous acid	$\text{HNO}_2, \text{Aq}$	308 „	
4. Nitric acid	$\text{HNO}_3, \text{Aq}$	491 „	
	$\text{N}_2\text{O}_5, \text{Aq}$	$2 \times 149$ „	
	$\text{HNO}_3$	419 „	Heat of solution 72 K
	$\text{N}_2\text{O}_5$	131 „	„ „ 167 „

The heat of fusion of nitrogen pentoxide is - 83 K, the heat of vaporisation - 48 K. The sum of these two equals the heat of formation of the solid pentoxide, so that the heat of formation of the gaseous pentoxide is nil.

5. Nitrogen peroxide		
	$\text{N}_2\text{O}_4$	- 26 K
	$\text{NO}_2$	- 77 „

The heat of dissociation of  $\text{N}_2\text{O}_4$  into  $2\text{NO}_2$  is - 129 K.

6. Nitric oxide	$\text{NO}$	- 216 K
7. Hydroxylamine	$\text{NH}_2\text{OH}, \text{Aq}$	244 „

### § 11. Phosphorus.

1. Phosphorus. The transformation of yellow phosphorus into red is accompanied by evolution of 273 K.

2. Phosphoric acid	$\text{H}_3\text{PO}_4$	3029 K
	$\text{H}_3\text{PO}_4, \text{Aq}$	3056 „
	$\text{P}_2\text{O}_5, \text{Aq}$	$2 \times 2030$ „

3. Phosphorous acid		
	$\text{H}_3\text{PO}_3$	2249 „
	$\text{H}_3\text{PO}_3, \text{Aq}$	2278 „
	$\text{P}_2\text{O}_3, \text{Aq}$	$2 \times 1252$ „

4. Hypophosphorous acid		
	$\text{H}_3\text{PO}_2$	1401 „
	$\text{H}_3\text{PO}_2, \text{Aq}$	1399 „
	$\text{P}_2\text{O}, \text{Aq}$	$2 \times 373$ „

5. Hydrogen phosphide	$\text{PH}_3$	43 „
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6. Phosphonium iodide	$\text{PH}_4\text{I}$	222 „
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7. Phosphorus trichloride	$\text{PCl}_3$	755 „	Heat of vaporisation - 69 K
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8. Phosphorus pentachloride	$\text{PCl}_5$	1051 „
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9. Phosphorus oxychloride	$\text{POCl}_3$	1460 „
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10. Phosphorus tribromide	$\text{PBr}_3$	448 „
---------------------------	----------------	-------

11. Phosphorus pentabromide	$\text{PBr}_5$	591 „
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Heat of Formation.

12. Phosphorus oxybromide  $\text{POBr}_3$  1056 K13. Phosphorus iodide  $\text{PI}_2$  99 „§ 12. **Arsenic.**

- |                        |                                     |                   |                                |
|------------------------|-------------------------------------|-------------------|--------------------------------|
| 1. Arsenic acid        | $\text{As}_2\text{O}_5$             | 2194 „            | Heat of solution 60 K          |
|                        | $\text{As}_2\text{O}_5, \text{Aq}$  | $2 \times 1127$ „ |                                |
|                        | $\text{H}_3\text{AsO}_4, \text{Aq}$ | 2153 „            |                                |
| 2. Arsenious acid      | $\text{As}_2\text{O}_3$             | 1547 „            | „ „ - 76 „                     |
|                        | $\text{As}_2\text{O}_3, \text{Aq}$  | $2 \times 735$ „  |                                |
| 3. Hydrogen arsenide   | $\text{AsH}_3$                      | - 441 „           |                                |
| 4. Arsenic trichloride | $\text{AsCl}_3$                     | 715 „             | Heat of vaporisation<br>- 84 K |
| 5. Arsenic tribromide  | $\text{AsBr}_3$                     | 449 „             |                                |
| 6. Arsenic tri-iodide  | $\text{AsI}_3$                      | 127 „             |                                |

§ 13. **Antimony.**

- |                           |                         |                         |
|---------------------------|-------------------------|-------------------------|
| 1. Antimony trichloride   | $\text{SbCl}_3$         | 914 „                   |
| 2. Antimony pentachloride | $\text{SbCl}_5$         | 1049 „                  |
| 3. Antimony trioxide      | $\text{Sb}_2\text{O}_3$ | 1660 „                  |
| 4. Antimony pentoxide     | $\text{Sb}_2\text{O}_5$ | 2228 „ (hydrated oxide) |

§ 14. **Boron.**

- |                      |                                   |        |
|----------------------|-----------------------------------|--------|
| 1. Boron trichloride | $\text{BCl}_3$                    | 1040 „ |
| 2. Boron trioxide    | $\text{B}_2\text{O}_3$            | 3172 „ |
|                      | $\text{B}_2\text{O}_3, \text{Aq}$ | 3352 „ |

The numbers are for amorphous boron and are not very trustworthy.

§ 15. **Carbon.**

The different modifications of carbon—diamond, graphite, and amorphous carbon—contain very different amounts of energy. The greatest is possessed by charcoal,—graphite has about 36 K less. Charcoal therefore evolves 36 K more on combustion than graphite. Two determinations only have been made for diamond, one gives 24 K the other 37 K less than charcoal; which of the two is the more correct is difficult to decide.

- |                    |               |                               |
|--------------------|---------------|-------------------------------|
| 1. Carbon dioxide  | $\text{CO}_2$ | 970 K (from amorphous carbon) |
| 2. Carbon monoxide | $\text{CO}$   | 290 „                         |

It is somewhat surprising that the first oxygen atom that combines with the carbon evolves much less heat than the second, the numbers being 290 and 680. It has been suggested that the two heats of combination are really equal, and that the difference of 390 K only serves to transform solid carbon into the gaseous state.

		Heat of Formation.
3. Methane	$\text{CH}_4$	218 K
4. Carbonyl chloride	$\text{COCl}_2$	551 „
5. Carbon tetrachloride	$\text{CCl}_4$	210 „
6. Carbonyl sulphide	$\text{COS}$	370 „
7. Carbon disulphide	$\text{CS}_2$	- 196 „

The heat of formation of carbon disulphide is negative, *i.e.* carbon burns in sulphur with absorption of heat.

§ 16. **Silicon.**

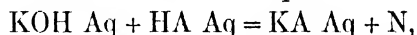
Crystalline silicon contains 91 K more energy than amorphous silicon. The heat of formation of all the silicon compounds is still very uncertain, so that the values found need not be given here.

## CHAPTER V

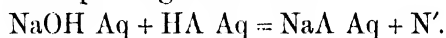
### THERMOCHEMISTRY OF THE METALS

THE heats of formation of the metallic salts in aqueous solution, which obey Hess's law of thermoneutrality, are also so related to each other that the corresponding differences are equal. Thus, for instance, the heats of formation of all the potassium salts are about 48 K greater than those of the corresponding sodium salts, and in the same way the heat of formation of the chlorides exceeds that of the iodides by 262 K.

This simple and tolerably general relation follows from Hess's Law. The heat of formation of the potassium salt KA, where A is any acid radical, can be calculated from the equation



if the heat of formation of potash, of the acid, and of water be known; N is the heat of neutralisation. Let us compare with this the heat of formation of the corresponding sodium salt—



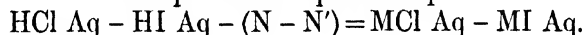
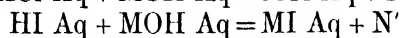
By subtraction we get



or  $\text{KOH Aq} - \text{NaOH Aq} - (\text{N} - \text{N}') = \text{KA Aq} - \text{NaA Aq}.$

The last equation signifies that the difference of the heats of formation of the hydroxides minus the difference of the heats of neutralisation is equal to the difference of the heats of formation of the salts. The first is the same for all potassium and sodium salts; and according to Hess's Law the differences between the heats of neutralisation of two bases with all acids are equal, so that the difference of the heats of formation of the salts must be independent of the acid they contain.

A perfectly similar proof holds for salts of the same metal with different acids—





Here the two differences on the left side are independent of the metal, and this must therefore be the case with the right side also.

From this relation we can deduce the heat of formation of a great number of different substances, once the characteristic differences have been calculated. It must not, however, be forgotten that Hess's Law is not a perfectly general one. It does not, for example, hold good in the case of mercury and cadmium compounds, nor does it when any solid participates in the reaction. For such substances, then, special measurements must always be made. The results of immediate measurement are therefore brought together in the following tables. Where such are wanting the relations just discussed may be employed to obtain results in most cases very near the real values. The numbers, as before, are the heats of formation of the substances from the elements.

### § 1. Potassium.

			Heat of Formation.	Heat of Solution.
1.	Potassium hydroxide	KOH	1032 K	133 K
2.	" monoxide	K <sub>2</sub> O, Aq	1646 "	
3.	" chloride	KCl	1043 "	- 44 "
4.	" chlorate	KClO <sub>3</sub>	959 "	
5.	" perchlorate	KClO <sub>4</sub>	1131 "	- 121 "
6.	" bromide	KBr	951 "	- 51 "
7.	" bromate	KBrO <sub>3</sub>	841 "	- 98 "
8.	" iodide	KI	801 "	- 51 "
9.	" iodate	KIO <sub>3</sub>	1245 "	- 68 "
10.	" sulphide	K <sub>2</sub> S	1012 "	100 "
11.	" hydrogen sulphide	KHS	585 "	6 "
12.	" sulphite	K <sub>2</sub> SO <sub>3</sub>	2738 "	14 "
13.	" pyrosulphite	K <sub>2</sub> S <sub>2</sub> O <sub>5</sub>	3716 "	- 112 "
14.	" sulphate	K <sub>2</sub> SO <sub>4</sub>	3446 "	- 64 "
15.	" hydrogen sulphate	KHSO <sub>4</sub>	2775 "	- 38 "
16.	" pyrosulphate	K <sub>2</sub> S <sub>2</sub> O <sub>7</sub>	3115 "	- 38 "
17.	" nitrate	KNO <sub>3</sub>	1195 "	- 85 "
18.	" carbonate	K <sub>2</sub> CO <sub>3</sub>	2811 "	65 "
19.	" hydrogen carbonate	KHCO <sub>3</sub>	2356 "	- 53 "

### § 2. Sodium.

1.	Sodium hydroxide	NaOH	1019 "	99 "
2.	" monoxide	Na <sub>2</sub> O	804 "	550 "
3.	" chloride	NaCl	976 "	- 12 "
4.	" hypochlorite	NaOCl, Aq	834 "	
5.	" chlorate	NaClO <sub>3</sub>	868 "	- 56 "
6.	" bromide	NaBr	858 "	- 2 "
7.	" iodide	NaI	691 "	12 "
8.	" sulphide	Na <sub>2</sub> S	870 "	150 "
9.	" hydrogen sulphide	NaHS	540 "	44 "

			Heat of Formation.	Heat of Solution.
10.	Sodium thiosulphate	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{aq}$	2652 K	- 114 K
11.	„ sulphite	$\text{Na}_2\text{SO}_3$	2685 „	- 111 „
12.	„ sulphate	$\text{Na}_2\text{SO}_4$	3288 „	2 „
13.	„ hydrogen sulphate	$\text{NaHSO}_4$	2678 „	- 12 „
14.	„ nitrate	$\text{NaNO}_3$	1113 „	- 50 „
15.	„ phosphate	$\text{Na}_2\text{HPO}_4$	4109 „	56 „
16.	„ carbonate	$\text{Na}_2\text{CO}_3$	2726 „	56 „
17.	„ hydrogen carbonate	$\text{NaHCO}_3$	2299 „	- 43 „

### § 3. Ammonium.

1.	Ammonium chloride	$\text{NH}_4\text{Cl}$	758 „	- 40 „
2.	„ bromide	$\text{NH}_4\text{Br}$	654 „	- 44 „
3.	„ iodide	$\text{NH}_4\text{I}$	493 „	- 35 „
4.	„ sulphate	$(\text{NH}_4)_2\text{SO}_4$	2822 „	- 26 „
5.	„ nitrate	$\text{NH}_4\text{NO}_3$	880 „	- 62 „

### § 4. Lithium.

1.	Lithium hydroxide	$\text{LiOH}, \text{Aq}$	1174 „	
2.	„ chloride	$\text{LiCl}$	938 „	84 „
3.	„ sulphate	$\text{Li}_2\text{SO}_4$	3342 „	60 „
4.	„ nitrate	$\text{LiNO}_3$	1116 „	3 „

### § 5. Barium.

No thermochemical experiment is known in which the metal barium itself is involved. Thomsen, however, has made it seem probable that the heat of formation of barium hydroxide is 1940 K. If we assume this provisional value to be correct, we can use the heats of formation calculated from it just as we do the others, being certain of committing no error so long as we keep away from questions where metallic barium must be taken into consideration. To denote the provisional character of the numbers, however, an asterisk has been affixed to them.

		Heat of Formation.	Heat of Solution.	
1.	Barium hydroxide	Ba(OH) <sub>2</sub>	2149* K	122 K
2.	„ monoxide	BaO	1242* „	345 „
3.	„ dioxide	BaO <sub>2</sub>	1416* „	
4.	„ chloride	BaCl <sub>2</sub>	1947* „	21 „
5.	„ chlorate	Ba(ClO <sub>3</sub> ) <sub>2</sub>	1450* „	– 67 „
6.	„ bromide	BaBr <sub>2</sub>	1700* „	50 „
7.	„ sulphide	BaS	983* „	
8.	„ sulphate	BaSO <sub>4</sub>	3381* „	
9.	„ nitrite	Ba(NO <sub>2</sub> ) <sub>2</sub>	1787* „	– 57 „
10.	„ nitrate	Ba(NO <sub>3</sub> ) <sub>2</sub>	2262* „	– 94 „
11.	„ carbonate	BaCO <sub>3</sub>	2834* „	

§ 6. **Strontium.**

§ 6. <b>Strontium.</b>		Heat of Formation.	Heat of Solution.	
1.	Strontium hydroxide	$\text{Sr}(\text{OH})_2$	2145 K	116 K
2.	„ oxide	$\text{SrO}$	1284 „	294 „
3.	„ chloride	$\text{SrCl}_2$	1846 „	111 „
4.	„ bromide	$\text{SrBr}_2$	1577 „	101 „
5.	„ sulphide	$\text{SrS}$	974 „	
6.	„ sulphate	$\text{SrSO}_4$	3309 „	
7.	„ nitrate	$\text{Sr}(\text{NO}_3)_2$	2198 „	- 46 „
8.	„ carbonate	$\text{SrCO}_3$	2812 „	

§ 7. **Calcium.**

1.	Calcium hydroxide	$\text{Ca}(\text{OH})_2$	2149 „	30 „
2.	„ oxide	$\text{CaO}$	1310 „	Heat of Hydration. 155 K
3.	„ chloride	$\text{CaCl}_2$	1698 „	Heat of Solution. 174 K
4.	„ bromide	$\text{CaBr}_2$	1409 „	25 „
5.	„ iodide	$\text{CaI}_2$	1073 „	277 „
6.	„ sulphide	$\text{CaS}$	896 „	
7.	„ sulphate	$\text{CaSO}_4$	3184 „	47 „
8.	„ nitrate	$\text{Ca}(\text{NO}_3)_2$	2026 „	40 „
9.	„ carbonate	$\text{CaCO}_3$	2704 „	

The transformation of arragonite into calc spar is accompanied by an evolution of some 24 K.

§ 8. **Magnesium.**

1.	Magnesium hydroxide	$\text{Mg}(\text{OH})_2$	2173 K	
2.	„ oxide	$\text{MgO}$	1439 „	
3.	„ chloride	$\text{MgCl}_2$	1510 „	359 K
4.	„ sulphide	$\text{MgS}$	776 „	
5.	„ sulphate	$\text{MgSO}_4$	3023 „	203 „
6.	„ nitrate	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{aq}$	2105 „	- 42 „

§ 9. **Aluminium.**

1.	Aluminium hydroxide	$\text{Al}(\text{OH})_3$	2970 „	
2.	„ chloride	$\text{AlCl}_3$	1610 „	768 „
3.	„ bromide	$\text{AlBr}_3$	1197 „	853 „
4.	„ iodide	$\text{AlI}_3$	704 „	890 „
5.	„ sulphide	$\text{Al}_2\text{S}_3$	1224 „	

§ 10. **Manganese.**

1.	Manganous hydroxide	$\text{Mn}(\text{OH})_2$	1632 „	
2.	„ chloride	$\text{MnCl}_2$	1120 „	160 „
3.	„ sulphide	$\text{MnS.aq}$	444 „	

		Heat of Formation.	Heat of Solution.
4. Manganous sulphate	$\text{MnSO}_4$	2499 K	138 K
5. „ carbonate	$\text{MnCO}_3$	2108 „	
6. Potassium permanganate	$\text{KMnO}_4$	1950 „	- 104 „

§ 11. **Iron.**

1. Ferrous hydroxide	$\text{Fe(OH)}_2$	1367 „	
2. Ferric „	$\text{Fe(OH)}_3$	1982 „	
3. Ferrosoferric oxide	$\text{Fe}_3\text{O}_4$	2647 „	
4. Ferrous chloride	$\text{FeCl}_2$	821 „	179 „
5. Ferric „	$\text{FeCl}_3$	961 „	633 „
6. Ferrous bromide	$\text{FeBr}_2, \text{Aq}$	808 „	
7. Ferric „	$\text{FeBr}_3, \text{Aq}$	968 „	
8. Ferrous iodide	$\text{FeI}_2, \text{Aq}$	464 „	
9. „ sulphide	$\text{FeS}, \text{aq}$	238 „	
10. „ sulphate	$\text{FeSO}_4, \text{Aq}$	2356 „	
11. Ferric sulphate	$\text{Fe}_2(\text{SO}_4)_3, \text{Aq}$	6184 „	

Carbon is taken up by iron (in cast iron) with absorption, silicon with evolution of heat.

§ 12. **Cobalt.**

1. Cobaltous hydroxide	$\text{Co(OH)}_2$	1318 K	
2. „ chloride	$\text{CoCl}_2$	765 „	183 K
3. „ sulphide	$\text{CoS}, \text{aq}$	197 „	
4. „ sulphate	$\text{CoSO}_4, \text{Aq}$	2305 „	

§ 13. **Nickel.**

1. Nickel hydroxide	$\text{Ni(OH)}_2$	1292 „	
2. „ chloride	$\text{NiCl}_2$	745 „	192 „
3. „ sulphide	$\text{NiS}, \text{aq}$	174 „	
4. „ sulphate	$\text{NiSO}_4, \text{Aq}$	2294 „	

§ 14. **Zinc.**

1. Zinc oxide	$\text{ZnO}$	858 „	
2. „ hydroxide	$\text{Zn(OH)}_2$	1511 „	
3. „ chloride	$\text{ZnCl}_2$	972 „	156 „
4. „ bromide	$\text{ZnBr}_2$	760 „	150 „
5. „ iodide	$\text{ZnI}_2$	492 „	113 „
6. „ sulphide	$\text{ZnS}, \text{aq}$	396 „	
7. „ sulphate	$\text{ZnSO}_4$	2300 „	185 „
8. „ nitrate	$\text{Zn(NO}_3)_2, \text{Aq}$	1323 „	

§ 15. **Cadmium.**

1. Cadmium hydroxide	$\text{Cd(OH)}_2$	1341 „	
2. „ chloride	$\text{CdCl}_2$	932 „	30 „

		Heat of Formation.	Heat of Solution.
3. Cadmium bromide	$\text{CdBr}_2$	752 K	4 K
4. „ iodide	$\text{CdI}_2$	488 „	- 10 „

The halogen compounds of cadmium do not obey the law of thermoneutrality; the heats of neutralisation for two equivalents of hydrochloric, hydrobromic, and hydriodic acid are respectively 203, 215, and 242 K, instead of being equal, as is the case with most of the corresponding salts.

5. Cadmium sulphide	$\text{CdS.aq}$	324 K	
6. „ sulphate	$\text{CdSO}_4$	2212 „	107 K
7. „ nitrate	$\text{Cd}(\text{NO}_3)_2.\text{Aq}$	1161 „	
8. „ carbonate	$\text{CdCO}_3$	1819 „	

#### § 16. Copper.

1. Cupric oxide	$\text{CuO}$	372 „	
2. Cuprous „	$\text{Cu}_2\text{O}$	408 „	
3. Cupric chloride	$\text{CuCl}_2$	516 „	111 „
4. Cuprous „	$\text{Cu}_2\text{Cl}_2$	657 „	
5. Cupric bromide	$\text{CuBr}_2$	326 „	83 „
6. Cuprous „	$\text{Cu}_2\text{Br}_2$	500 „	
7. Cuprous iodide	$\text{Cu}_2\text{I}_2$	325 „	
8. „ sulphide	$\text{Cu}_2\text{S}$	183 „	
9. Cupric sulphate	$\text{CuSO}_4$	1826 „	158 „
10. „ nitrate	$\text{Cu}(\text{NO}_3)_2.\text{Aq}$	823 „	

#### § 17. Mercury.

By choosing an unsuitable method, Thomsen obtained for the heat of formation of the mercury compounds values which were affected by a considerable error. Nernst (1888) has made more accurate determinations. It is necessary to refer to this fact, as from the use of the older numbers there have repeatedly arisen difficulties and contradictions which entirely disappear with the new values.

1. Mercurous oxide	$\text{Hg}_2\text{O}$	222 K	
2. Mercuric „	$\text{HgO}$	207 „	
3. Mercurous chloride	$\text{Hg}_2\text{Cl}_2$	626 „	
4. Mercuric „	$\text{HgCl}_2$	532 „	- 33 K
5. Mercurous bromide	$\text{Hg}_2\text{Br}_2$	405 „	
6. Mercuric „	$\text{HgBr}_2$	160 „	
7. Mercurous iodide	$\text{Hg}_2\text{I}_2$	284 „	
8. Mercuric „	$\text{HgI}_2$	243 „	

The halogen compounds of mercury, like those of cadmium, do not obey the law of thermoneutrality.

- |                      |              |      |
|----------------------|--------------|------|
| 9. Mercuric sulphide | $\text{HgS}$ | 49 K |
|----------------------|--------------|------|
10. Amalgams. The alkali metals combine with mercury with great

evolution of heat. Solid potassium amalgam,  $\text{KHg}_{12}$  has a heat of formation of 340 K ; sodium amalgam,  $\text{NaHg}_6$ , 211 K. As potassium on combining with mercury evolves much more heat than sodium, sodium amalgam acting on water or acids gives out about 60 K more than potassium amalgam.

### § 18. Silver.

		Heat of Formation.	Heat of Solution.
1. Silver oxide	$\text{Ag}_2\text{O}$	59 K	
2. „ chloride	$\text{AgCl}$	294 „	
3. „ bromide	$\text{AgBr}$	227 „	
4. „ iodide	$\text{AgI}$	138 „	
5. „ sulphide	$\text{Ag}_2\text{S}$	33 „	
6. „ sulphate	$\text{Ag}_2\text{SO}_4$	1673 „	- 45 K
7. „ carbonate	$\text{Ag}_2\text{CO}_3$	1229 „	
8. „ nitrate	$\text{AgNO}_3$	287 „	- 54 „

### § 19. Thallium.

1. Thallous oxide	$\text{Tl}_2\text{O}$	423 „	- 31 „
2. „ hydroxide	$\text{TlOH}$	570 „	- 32 „
3. „ chloride	$\text{TlCl}$	486 „	- 101 „
4. „ bromide	$\text{TlBr}$	413 „	
5. „ iodide	$\text{TlI}$	302 „	
6. „ sulphide	$\text{Tl}_2\text{S}$	197 „	
7. „ sulphate	$\text{Tl}_2\text{SO}_4$	2210 „	- 83 „
8. „ nitrate	$\text{TlNO}_3$	582 „	- 100 „
9. Thallous hydroxide	$\text{Tl(OH)}_3$	1458 „	
10. „ bromide	$\text{TlBr}_3, \text{Aq}$	564 „	

### § 20. Lead.

1. Lead oxide	$\text{PbO}$	503 „	
2. „ chloride	$\text{PbCl}_2$	828 „	- 68 „
3. „ bromide	$\text{PbBr}_2$	645 „	- 100 „
4. „ iodide	$\text{PbI}_2$	398 „	
5. „ sulphide	$\text{PbS}$	183 „	
6. „ sulphate	$\text{PbSO}_4$	2162 „	
7. „ nitrate	$\text{Pb(NO}_3)_2$	1055 „	- 76 „
8. „ carbonate	$\text{PbCO}_3$	729 „	

### § 21. Bismuth.

1. Bismuth trichloride	$\text{BiCl}_3$	908 „	
2. „ oxychloride	$\text{BiOCl}$	882 „	
3. „ hydroxide	$\text{Bi(OH)}_3$	1717 „	

### § 22. Tin.

1. Stannous hydroxide	$\text{Sn(OH)}_2$	1365 „	
2. „ chloride	$\text{SnCl}_2$	808 „	3 „
3. Stannic chloride	$\text{SnCl}_4$	1273 „	299 „

§ 23. **Gold.**

The gold precipitated from solution comes down in different modifications with variations of energy from 32 K to 47 K. The following numbers refer to the variety with most energy, viz. that precipitated by sulphur dioxide from the chloride.

		Heat of Formation.	Heat of Solution.
1. Auric hydroxide	$\text{Au}(\text{OH})_3$	960 K	
	$\text{Au}_2\text{O}_3, \text{aq}$	- 132 „	
2. Auric chloride	$\text{AuCl}_3$	228 „	45 K
3. Chlorauric acid	$\text{HAuCl}_4, \text{Aq}$	713 „	
4. Auric bromide	$\text{AuBr}_3, \text{Aq}$	51 „	
5. Bromauric acid	$\text{HAuBr}_4, \text{Aq}$	412 „	
6. Aurous chloride	$\text{AuCl}$	58 „	
7. „ bromide	$\text{AuBr}$	- 1 „	
8. „ iodide	$\text{AuI}$	- 55 „	

§ 24. **Platinum.**

1. Chloroplatinic acid	$\text{H}_2\text{PtCl}_6, \text{Aq}$	1632 „
2. Bromoplatinic „	$\text{H}_2\text{PtBr}_6, \text{Aq}$	1138 „

The heats of neutralisation of the two acids are the same as that of hydrochloric acid.

3. Chloroplatinous acid	$\text{H}_2\text{PtCl}_4, \text{Aq}$	1202 K
4. Bromoplatinous „	$\text{H}_2\text{PtBr}_4, \text{Aq}$	884 „
5. Platinous hydroxide	$\text{Pt}(\text{OH})_2$	863 „

§ 25. **Palladium.**

1. Palladious hydroxide	$\text{Pd}(\text{OH})_2$	911 „
2. Chloropalladious acid	$\text{H}_2\text{PdCl}_4, \text{Aq}$	1265 „
3. Palladious iodide	$\text{PdI}_2$	182 „
4. Palladic hydroxide	$\text{Pd}(\text{OH})_4$	1672 „

## CHAPTER VI

### ORGANIC COMPOUNDS

THE thermochemistry of organic compounds is rendered specially interesting by the circumstance that most of the energy used in the industrial arts, as well as all the energy of living organisms, is got from the combustion of organic compounds. The accurate comprehension therefore of the economy of these working systems must be preceded by a knowledge of the amount of energy contained in the substances which come under consideration.

Unfortunately the special peculiarity of the processes between carbon compounds, which almost without exception take place slowly, or under pressure at high temperatures, has restricted any extensive research in this domain. There is practically only one method for the determination of the energy in organic compounds, just as there is but one in organic analysis, and that method is the same in both cases, viz. complete combustion. The heat here appearing is the same as that taken into consideration in the first instance in the technical or physiological utilisation of organic substances, and thus the heat of combustion plays a very important part.

If the heat of combustion of an organic compound be subtracted from those of its elements, we obtain, according to the fundamental principle of energy, the heat of combination of the compound from its elements. This has merely an arithmetical significance, as we have scarcely ever been able to form organic compounds directly from their elements. For the purpose of calculating heats of reaction the heats of combustion can, however, be used just as well, for the difference of the heats of combustion of the substances before and after the reaction is equal to the heat developed by the reaction itself, as can also be easily shown from the fundamental principle.

The heat of formation of organic compounds differs according to the form of carbon taken. Berthelot calculates from diamond. As the heat of combustion of this substance, however, has been determined by two experiments only, these two differing by 20 K, the basis of this calculation seems not sufficiently secure. It would therefore perhaps



be better to refer the heats of formation to amorphous carbon, the heat of combustion of which has been accurately determined from a good number of concordant experiments. In principle, of course, it makes no difference which we choose. The numbers which follow are calculated with respect to amorphous carbon.

The combustion of organic bodies first reached an advanced stage of development in the hands of Favre and Silbermann (1852). These chemists conducted the combustion in a metal chamber supplied with oxygen; the substance to be burned was, according to its nature, contained in a little basket or in a small lamp, and the gases produced on the combustion were led through a long metal worm, which, along with the combustion chamber itself, was immersed in the water of a large calorimeter.

The method was afterwards modified in various ways. With due care it gives good results, but it is very difficult to conduct the combustion so that it shall be quite complete.

A second method, introduced by Frankland (1866), and perfected by Stohmann (1879), is now almost entirely abandoned. It consists in mixing the substance with potassium chlorate and letting the mixture burn in a bell-jar under the water of the calorimeter. The experiments are difficult to perform and often miscarry.

Berthelot, finally, has worked out (1881 and 1884) a method according to which the substance is burnt in a stout-walled vessel lined with platinum, and filled with strongly compressed oxygen (Fig. 49). Ignition is brought about by an electric spark, or by heating a thin iron wire to incandescence by means of an electric current, and allowing its glowing products of combustion to drop on the substance. The whole "calorimetric bomb" is covered by the water of a calorimeter. This method has the merit that the experiments take up but little time and are almost always successful, but, on the other hand, it requires extensive and costly apparatus.

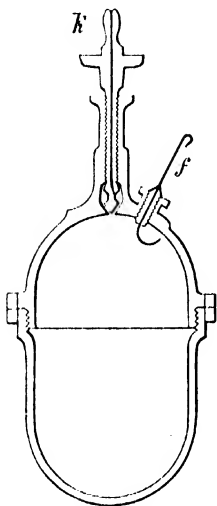


FIG. 49.

In the calculation of the experimental results it must be borne in mind that both the oxygen necessary for the combustion and the carbonic acid which is formed, are in the gaseous state. In consequence of the disappearance of the former, heat is developed by the external air entering to take its place. The amount of this is  $2 T$  cal. per gram-molecular-weight (p. 72), or in the calories here employed  $\cdot 02 \times T$ ; at  $18^\circ$  this is  $5.82 K$ . To reduce the heats of combustion to constant volume we must therefore add  $5.82 K$  for each molecule of oxygen used in the combustion, and subtract  $5.82 K$  for each molecule of carbon dioxide (or of any other gas) formed.

We must also take into consideration the state of aggregation of the substances investigated. For reducing to the gaseous state we have the

approximate rule that the heat of vaporisation at the boiling-point  $T$  (measured on the absolute scale of temperature) is about  $- \cdot 25 T$ . The rule is accurate within about ten per cent, and serves at least for preliminary calculations.

The influence of the solid condition of the substance is not so easy to eliminate, as the relations between the heat of fusion and the nature of the substance (as well as other circumstances) have not yet been made clear. The amount varies very much, from a few up to 50 K.

Before we proceed to the numerical values in the following pages, it is necessary to state that a great number of them have been recently called in question. The various investigators are at present engaged in a controversy as to the relative accuracy of the methods adopted by them, a controversy which, in whatever way it may finally be settled, at least shows that errors of several per cent in the heats of combustion have been made on one side or the other. The numbers which follow are therefore only to be used within such limits of error.

The following heats of combustion have been found for the hydrocarbons of the methane series—

		Difference.
$\text{CH}_4$	2119 K	
$\text{C}_2\text{H}_6$	3704 „	1585 K
$\text{C}_3\text{H}_8$	5292 „	1588 „
$\text{C}_4\text{H}_{10}$	6872 „	1580 „
$\text{C}_5\text{H}_{12}$	8471 „	1599 „
$\text{C}_6\text{H}_{14}$	9992 „	1521 „

The difference between the heats of combustion of neighbouring homologous hydrocarbons is very nearly constant.

† To calculate the heat of formation, we have, for example, the heat of combustion of the elements of methane,  $\text{CH}_4$ , equal to  $970 + 2 \times 683 = 2336$  K, and that of methane itself equal to 2119 K. The difference of 217 K is the heat of formation of methane from its elements.

For every addition of  $\text{CH}_2$  the heat of combustion increases on the average 1580 K. The heat of combustion of the elements is  $970 + 683 = 1653$  K. Consequently the heat of formation of a hydrocarbon increases by about 73 K for every  $\text{CH}_2$  added, and is in general for a hydrocarbon of the formula  $\text{C}_n\text{H}_{2n+2}$  equal to  $144 + n73$  K.

The unsaturated hydrocarbons of the ethylene group show the same difference in ascending the homologous series—

		Difference.
$\text{C}_2\text{H}_4$	3334 K	1593 K
$\text{C}_3\text{H}_6$	4927 „	1579 „
$\text{C}_4\text{H}_8$	6506 „	1590 „
$\text{C}_5\text{H}_{10}$	8076 „	

The heat of formation of the substances  $\text{C}_n\text{H}_{2n}$  is  $-173 + n73$  K. To form ethylene from its elements 27 K would be required.

Similar relations are found in other homologous series, *e.g.* in the alkyl chlorides and bromides, and in the alcohols. Thomsen thus gives—

			Difference.
Methyl chloride (gaseous)	1648 K		1571 K
Ethyl     "     "	3219 "		1583 "
Propyl    "     "	4802 "		1577 "
Isobutyl   "     "	6379 "		
<hr/>			
Methyl iodide (gaseous)	2015 K		1577 K
Ethyl     "     "	3592 "		

As the homologous differences of all these substances are equal, the differences between the heats of combustion or formation of the corresponding chlorine, bromine, and iodine compounds must also be approximately equal.

For the series of alcohols the heats of combustion determined by Thomsen are as follows—

			Difference.
Methyl alcohol (gaseous)	1822 K		1583 K
Ethyl     "     "	3405 "		1581 "
Propyl    "     "	4986 "		1599 "
Isobutyl   "     "	6585 "		1616 "
Isoamyl    "     "	8201 "		

Here again we have approximately equal differences; for the higher alcohols they increase somewhat, but it is not improbable that these values have been determined too high.

We can imagine ethyl alcohol to have been formed of ethylene and water. The heat of combustion of ethylene is 3334; that of water is 0. As ethyl alcohol has a somewhat greater heat of combustion, *viz.* 3405 K, the difference of 71 K must have appeared in the union of water with the ethylene, which union is therefore accompanied by an absorption of heat. This example shows how erroneous is the so-called "Welter's rule," according to which the heat of combustion of an organic compound is found by adding together those of the elements after removal of as much of the oxygen and hydrogen present as will go to form water.

The heat of combustion of the alcohols has also been investigated by Stohmann. His numbers, which are for the liquid state, are smaller than Thomsen's, the difference being greater than can be accounted for by the heat of vaporisation alone—

			Difference.
Methyl alcohol	1,685 K		1561 K
Ethyl     "     "	3,246 "		1565 "
Propyl    "     "	4,811 "		1565 "
Butyl     "     "	6,376 "		1558 "
Amyl     "     "	7,934 "		3 × 1566 "
Capryl    "     "	12,622 "		8 × 1561 "
Cetyl     "     "	25,109 "		

The general relation that the differences between the heats of combustion of homologous compounds are equal, is seen in these numbers also, which probably come nearer the truth than Thomsen's. That the constant difference is somewhat smaller may be accounted for by the increase of the heat of vaporisation with increasing molecular weight.

On the combustion of isomeric alcohols the same amount of heat is in general evolved. The numbers obtained by some investigators are abnormal, but the great majority of instances seem to show that isomeric compounds of identical or similar function contain very nearly the same quantity of energy, so that the thermal effect on their transformation one into the other is very small. Thomsen, for example, found 4986 and 4933 K for gaseous normal propyl and iso-propyl alcohol respectively. Luginin obtained 6367 and 6413 K for isobutyl alcohol and trimethylcarbinol; from the last number we should subtract the heat of fusion, which although not yet exactly known, must be about 40 K. In other cases greater differences have been found, but it is just there that the observations are contradictory amongst themselves.

Stohmann has furnished us with plentiful data for polyatomic alcohols and carbohydrates, his investigation being undertaken with reference to the thermal economy of animals.

		Heat of Combustion.	Heat of Formation.	Thermal Effect.
Erythrite	$C_4H_{10}O_4$	4,972 K	2324 K	- 408 K
Arabinose	$C_5H_{10}O_5$	5,542 „	2723 „	- 692 „
Mannite	$C_6H_{14}O_6$	7,169 „	3334 „	- 764 „
Dulcitol	$C_6H_{14}O_6$	7,113 „	3390 „	- 708 „
Dextrose	$C_6H_{12}O_6$	6,646 „	3274 „	- 824 „
Lactose	$C_6H_{12}O_6$	6,586 „	3334 „	- 754 „
Cane-sugar	$C_{12}H_{22}O_{11}$	13,222 „	5933 „	- 1580 „
Milk-sugar	$C_{12}H_{22}O_{11}$	13,259 „	5996 „	- 1519 „
Melittose	$C_{16}H_{32}O_{16}$	19,797 „	6651 „	- 4477 „
Arabic acid	$C_{12}H_{22}O_{11}$	13,694 „	5461 „	- 359 „
Cellulose	$C_6H_{10}O_5$	6,717 „	2519 „	- 897 „
Starch	$C_6H_{10}O_5$	6,679 „	2557 „	- 859 „
Inulin	$C_6H_{10}O_5$	6,593 „	2613 „	- 772 „

The numbers show that all these substances have a pretty high heat of formation. By subtracting the heat corresponding to the elements of water, we get the differences contained in the third column, or the "errors" of Welter's rule, which are here very considerable. If we imagine the carbohydrates to arise from the combination of carbon and water, the quantities of heat in the last column would be absorbed. On the other hand, when these substances undergo combustion in the animal organism, so much more heat is liberated than would be the case if the carbon were merely burned as such. This explains the fact, incomprehensible to the earlier physiologists, that the animal produces an apparent excess of heat over the quantity calculated from the carbonic acid evolved.

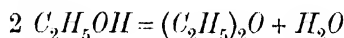
The same constant difference in the homologous series is seen with acids also. The following heats of combustion of the acetic series were determined by Stohmann, and refer to the liquid substances:—

			Difference.
Formic acid	$\text{CH}_2\text{O}_2$	590 K	
Acetic „	$\text{C}_2\text{H}_4\text{O}_2$	2,133 „	1543 K
Propionic „	$\text{C}_3\text{H}_6\text{O}_2$	3,679 „	1546 „
Butyric „	$\text{C}_4\text{H}_8\text{O}_2$	5,227 „	1548 „
Valerianic „	$\text{C}_5\text{H}_{10}\text{O}_2$	6,767 „	1540 „
Caproic „	$\text{C}_6\text{H}_{12}\text{O}_2$	8,312 „	1545 „
Caprylic „	$\text{C}_8\text{H}_{16}\text{O}_2$	11,400 „	$2 \times 1544$ „
Capric „	$\text{C}_{10}\text{H}_{20}\text{O}_2$	14,495 „	$2 \times 1548$ „
Lauric „	$\text{C}_{12}\text{H}_{24}\text{O}_2$	17,572 „	$2 \times 1539$ „
Myristic „	$\text{C}_{14}\text{H}_{28}\text{O}_2$	20,646 „	$2 \times 1532$ „
Palmitic „ (solid)	$\text{C}_{16}\text{H}_{32}\text{O}_2$	23,619 „	$2 \times 1487$ „
Stearic „ (solid)	$\text{C}_{18}\text{H}_{36}\text{O}_2$	26,778 „	$2 \times 1580$ „

Similar relations amongst other homologous substances have been often observed, but as they contain nothing new they need not be given here.

The substances derived from the combination of the alcohols with themselves, and with acids, with loss of water—the simple and compound ethers—have mostly a heat of combustion differing but little from the sum of the heats of combustion of their components, showing that these actions take place with very slight thermal change. The thermal change which does take place has often the negative sign, *i.e.* the substances absorb heat on combination.

Thus the heat of combustion of ethyl ether  $(\text{C}_2\text{H}_5)_2\text{O}$  is 6600 K, while twice that of alcohol is 6492 K—giving 108 K, for the process of etherification. The expelled water has here been supposed liquid, however, so that we ought to subtract its heat of vaporisation. We obtain then only 13 K for the heat of the following reaction—the substances being all gaseous



The numbers obtained from the comparison of the heats of combustion of the compound ethers and of the alcohols and acids are similar. The former are mostly from 10 to 20 K greater than the sum of the latter. This rule may be used to calculate with close approximation the heat of combustion of organic compounds formed with loss of the elements of water.

The aldehydes stand between the alcohols and the monobasic acids with the same number of carbon atoms, in respect of their heat of combustion. With them rank the ketones, even the somewhat distant type of isomerism between the two series having no decided effect on the heat of combustion. Thus we have for propionic aldehyde,  $\text{C}_2\text{H}_5\text{COH}$ , 4407 K, and for acetone,  $(\text{CH}_3)_2\text{CO}$ , 4373 K, both substances being in the gaseous state.

Very little of a general character can be said of the organic nitrogen compounds. It is remarkable that a considerable absorption of heat accompanies the formation of cyanogen from its elements. The heat of combustion of  $(\text{CN})_2$  is 2596 K, while that of two atoms of amorphous carbon is 1940 K; the considerable quantity of 656 K is thus taken up. In this respect cyanogen resembles acetylene, which likewise is formed at high temperatures with great absorption of heat (about 500 K, as the heat of combustion is from 3100 K to 3150 K).

When cyanogen combines with hydrogen, 107 K are evolved per atom of hydrogen. This number is near the number for hydrogen bromide. The heat of formation from the elements remains negative ( $-275$  K). That hydrogen cyanide behaves as an extremely weak acid has already been mentioned (p. 220).

Heat of combustion of the amine bases (Thomsen).

			Difference.
Methylamine	$\text{CH}_3\text{NH}_2$	2583 K	
Dimethylamine	$(\text{CH}_3)_2\text{NH}$	4205 „	1622 K
Trimethylamine	$(\text{CH}_3)_3\text{N}$	5286 „	1621 „

The difference for  $\text{CH}_2$  is rather greater than usual, but the compounds are not homologous in the real sense. If we compare the following—

			Difference.
Methylamine	$\text{CH}_3\text{NH}_2$	2583 K	
Ethylamine	$\text{C}_2\text{H}_5\text{NH}_2$	4157 „	1574 K
Propylamine	$\text{C}_3\text{H}_7\text{NH}_2$	5757 „	1600 „
Isobutylamine	$\text{C}_4\text{H}_9\text{NH}_2$	7254 „	1497 „
Amylamine	$\text{C}_5\text{H}_{11}\text{NH}_2$	8906 „	1652 „

we find somewhat varying differences, the mean, however, 1581, being equal to the constant of the preceding homologous series.

The heats of combustion of the nitrogenous final products of metabolism in the animal are given by Stohmann as follows—

Urea	$\text{CO}(\text{NH}_2)_2$	1,479 K
Uric acid	$\text{C}_5\text{H}_4\text{N}_4\text{O}_3$	4,404 „
Hippuric acid	$\text{C}_9\text{H}_9\text{NO}_3$	10,099 „

The heat of combustion of numerous aromatic compounds has also been determined. The chief results have exactly the same form as in the case of the fatty compounds, so that only a cursory notice is necessary.

The heat of combustion of benzene has had different values assigned to it. Thomsen found 8000 K for the gaseous substance, while Berthelot and Stohmann give considerably smaller values, viz. 7760 K and 7875 K. With the homologues of benzene we again see the increase of 1550 to 1580 K for each  $\text{CH}_2$ , the different isomers showing no great variation. A few heats of combustion, determined

by Stohmann, for other aromatic substances may serve to give a general idea of the relations here involved.

Phenol	$C_6H_6O$	7237 K
Pyrocatechin	$C_6H_6O_2$	{ 6682 ,,
Resorcin		{ 6708 ,,
Hydroquinone		{ 6701 ,,
Pyrogallol	$C_6H_6O_3$	{ 6163 ,,
Phloroglucin		{ 6176 ,,
o-Cresol	$C_7H_8O$	{ 8830 ,,
m-Cresol		{ 8810 ,,
p-Cresol		{ 8829 ,,
Anisol	$C_7H_8O$	9013 ,,
Benzoic acid	$C_7H_6O_2$	7663 ,,
,, aldehyde	$C_7H_6O$	8417 ,,
,, alcohol	$C_7H_8O$	8953 ,,
Methyl benzoate	$C_8H_{10}O$	9440 ,,
Phthalic acid	$C_8H_6O_4$	7570 ,,
Salicylic acid	$C_7H_6O_3$	7236 ,,
Methyl salicylate	$C_8H_8O_3$	8988 ,,
p-Oxybenzoic acid	$C_7H_6O_3$	7158 ,,
Methyl p-oxybenzoate	$C_8H_8O_3$	8892 ,,

The rules given above are here also generally obeyed. It is remarkable that while the three isomeric cresols,  $CH_3 \cdot C_6H_4 \cdot OH$ , have the same heat of combustion, the metameric anisol,  $C_6H_5 \cdot OCH_3$ , differs considerably from them. It is evident from the comparison of o-oxybenzoic acid (salicylic acid) with p-oxybenzoic acid that not all position-isomers have the same heat of combustion.

We may calculate the heats of combustion of the homologues of the above compounds with sufficient accuracy by adding 1550 K for every increase of  $CH_2$ .

## CHAPTER VII

### THE SECOND LAW OF THERMODYNAMICS

CHEMICAL energy, though the source of all physiological as well as of all technical work, cannot be transformed directly into such ;—for the most part heat, and sometimes electrical energy, appears as an intermediate form. It is therefore of importance to know the laws of the transformation of heat into other forms of energy.

A process, *i.e.* a change in the state or distribution of energy, only takes place when the intensity of the energy (p. 208) is different at two neighbouring situations. The intensity of heat is temperature ; all the power of doing work possessed by heat depends therefore on differences of temperature. No quantity of heat-energy, however great, can perform the smallest quantity of work when it is collected in a number of bodies all having the same temperature ; and we see at once that the quantity of heat transformable into work must increase proportionately with the disposable difference of temperature.

Further consideration shows that even the heat given up by a hot body while sinking to the temperature of neighbouring bodies cannot completely pass into mechanical energy. If we imagine, for instance, the system to consist of two bodies, say a hot iron and a cold mass of gas enclosed in a cylinder with a movable piston, then, if we bring the hot iron into the gas, the latter experiences a rise of temperature, expands, and performs the corresponding work. This, however, cannot take place otherwise than by the use of a portion of the additional heat to raise the temperature of the gas—a portion which is not and cannot be transformed into work. The fraction of the total heat transferred which can under the given circumstance be turned into work is called the economic coefficient.

This necessity, that a part of the heat employed to produce work must fall to a lower than its original temperature, was recognised by Sadi Carnot as early as 1824. It caused him to compare the passage of heat from a higher to a lower temperature with the fall of a weight, and in this fall to see the source of the work to be obtained from the heat.



At the present time such a conception is not tenable. We know that heat and work are of the same nature—are both, in fact, forms of energy, and that the one can only be produced when the proportionate quantity of the other disappears. In this point, therefore, Carnot's ideas were erroneous. But in spite of the error Carnot discovered another principle of decisive importance for the transformation—the law, namely, that the quantity of work obtainable under given circumstances from a certain quantity of heat is a function of the temperature only, being independent of the nature of the working substances and of the particular process employed.

The principle follows immediately from Carnot's wrong conception: just as the work obtainable from a quantity of water depends only on the fall, so the work got from the "fall of heat" can only be a function of the temperature. When the unsoundness of this reasoning came to be recognised, quite new considerations had to be introduced.

These we owe to Clausius, who stated the principle that heat cannot of itself pass from a cold to a hot body. This is a special case of the general principle that changes in the state of the energy of given systems can only take place when the intensities of the energies are different.

In order to prove on this new basis that the heat available for transformation into work depends only on the temperature, we consider a process in which the working substance after a series of suitable transformations finally comes back to its initial state. Such a process is called a cycle. It shall further be subject to the condition that every transference of heat or change of volume may equally well occur in the opposite sense, in other words, the differences of temperature and pressure must be infinitely small. Such a cycle is called reversible.\*

By means of these reversible cycles we can transform at pleasure work into heat, or heat into work. If, for example, a gas is allowed to expand at a high temperature and a correspondingly high pressure, thereby doing work, and is then cooled and compressed at a lower pressure, work being thereby done on it, the latter amount is less than the former, so that on the whole we obtain some work in excess. If the process be gone through in the reverse direction, more work is spent than is gained, and heat of a higher temperature is produced.

Let us now consider a reversible cycle of operations to be so performed, that at the higher temperature  $T_1$  the quantity of heat  $Q_1$  is supplied to the working substance, which again at the lower tempera-

\* The actual realisation of such reversible cycles would be of infinitely long duration. They are, therefore, only introduced as ideal limiting cases, just as in dynamics we speak of perfectly rigid solids, perfectly elastic bodies, etc., although these substances have no real existence.

ture  $T_2$  gives up the smaller quantity of heat  $Q_2$ . The quantity changed into work is then  $Q_1 - Q_2$ .

We now perform a second cycle between the same temperatures in such a way, that at the lower temperature  $T_2$ ,  $Q_2$  is communicated to the working substance; then we let so much work be spent upon it that the same quantity of heat is again given up at the higher temperature, but to this must be added the amount of heat corresponding to the work done, so that at  $T_1$  the total quantity of heat  $Q'_1$  is given up. The question arises as to how  $Q'_1$  is related to  $Q_1$ . Now  $Q'_1$  cannot be greater than  $Q_1$ , for then  $Q'_1 - Q_1$  would "of itself" have risen to a higher temperature, for after the completion of the two cycles all the substances are in their initial state.  $Q'_1$  might then, perhaps, be less than  $Q_1$ . But neither is this in accordance with the principle stated above, as we at once see if we consider the cycles to be performed in the reverse way, which according to our assumption may be done. For then  $Q'_1$  is communicated to the substance and does so much work that by its means the quantity  $Q_1$  (which is greater than  $Q'_1$ ) can be raised to the higher temperature. Here again we have heat "of itself" assuming a higher temperature, which is in contradiction to our principle. Nothing therefore remains but to conclude that  $Q_1 = Q'_1$ , *i.e.* that the ratio of the heat transformable into work to the whole heat transferred is in such reversible cycles independent of the nature of the process and of the working substance, and is determined only by the temperatures between which the substance works.

It is, therefore, only necessary to determine this ratio for any one process in order to establish it quite generally. Gases are best suited to our purpose, as the relations obtaining with them are most easily studied. We allow a quantity of gas (say 2 g. of hydrogen) to perform the following cycle, which we represent graphically by Fig. 50.

Let the gas at first have the pressure  $p_1$  and the volume  $v_1$  at the temperature  $T_1$ . We allow it to expand a little,

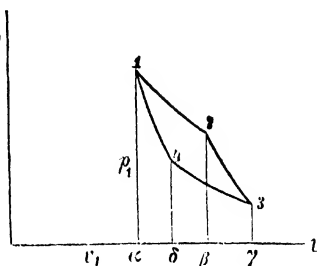


FIG. 50.

the temperature remaining constant; it is necessary for this purpose that a quantity of heat  $Q_1$  corresponding to the work should be communicated to it. Pressure and volume are then  $p_2$  and  $v_2$ . Next let us remove the source of heat and allow the gas to expand further. Here again it performs work, but receiving no heat from external sources, it must expand its own heat and therefore grow colder: let the temperature it reaches be  $T'$ , the pressure and volume being  $p_3$  and  $v_3$ . We now compress the gas. Work is required for this; let us remove the heat as it is produced so that the temperature  $T'$  is retained, the

pressure and volume, however, becoming  $p_4$  and  $v_4$ . Finally, let us isolate the gas and compress it further. The heat produced remains in the gas and raises its temperature, and the last part of the process is so arranged that when the gas reaches the initial temperature  $T$  it shall also have the initial pressure and volume  $p_1$  and  $v_1$ —an arrangement always possible.

The work done by the gas in this cycle is represented by the curvilinear quadrilateral 1 2 3 4. This work, namely, is always the product of pressure and change of volume of the gas, so that the surface  $\alpha$  1 2  $\beta$  represents the work for the passage from 1 to 2, it being always decomposable into as many small strips as we please, whose height is the pressure and whose breadth is the very small change of volume. In the same way  $\beta$  2 3  $\gamma$  is numerically equal to the work from 2 to 3; from 3 to 4 we have the work  $\delta$  4 3  $\gamma$ ; and from 4 to 1, lastly,  $\alpha$  1 4  $\delta$ . If the sum of the two last is subtracted from the sum of the two first, the quadrilateral 1 2 3 4 remains as measure of the work done in the whole cycle.

Now the work which a gas can perform by expanding from the volume  $v_1$  to the volume  $v_2$ , the temperature  $T$  remaining constant, is given by  $RT \lg \frac{v_1}{v_2}$  (p. 71),  $R$  being the gas-constant (equal in thermal measurement to 2 cal. for a gram-molecular-weight). Consequently the heat  $Q$  to be communicated in this part of the cycle is equal to  $2T \lg \frac{v_1}{v_2}$ , the gas requiring no heat for mere change of volume. From 2 to 3 no heat is taken up according to our assumption. The gas on being compressed from 3 to 4, gives up a quantity of heat  $Q'$ , specified by a similar formula,  $Q' = 2T' \lg \frac{v_4}{v_3}$ . Between 4 and 1 again no heat enters or leaves the substance.

Consequently the ratio of the heat taken up,  $Q$ , to the heat given out,  $Q'$ , is

$$\frac{Q}{Q'} = \frac{T \lg \frac{v_1}{v_2}}{T' \lg \frac{v_4}{v_3}}.$$

For the processes 2, 3 and 4, 1, the formula developed on p. 74, holds good, as heat neither enters nor leaves the system; so that

$$\left(\frac{v_2}{v_3}\right)^k = \frac{p_3}{p_2} \text{ and } \left(\frac{v_1}{v_4}\right)^k = \frac{p_4}{p_1}.$$

Now  $p v = RT$ , and in particular  $p_2 v_2 = RT$  and  $p_3 v_3 = RT'$ . Thus  $\frac{p_3}{p_2} = \frac{v_2}{v_3} \cdot \frac{T'}{T}$ , and similarly  $\frac{p_4}{p_1} = \frac{v_1}{v_4} \cdot \frac{T'}{T}$ . By substituting these values in

the equations we get after a slight transformation

$$\left(\frac{v_2}{v_3}\right)^{k-1} = \frac{T'}{T} \text{ and } \left(\frac{v_1}{v_4}\right)^{k-1} = \frac{T'}{T},$$

*i.e.*

$$\frac{v_2}{v_3} = \frac{v_1}{v_4} \text{ or } \frac{v_1}{v_2} = \frac{v_4}{v_3},$$

which was to be proved. In this way the ratio of the two quantities of heat comes to be

$$\frac{Q}{Q'} = \frac{T}{T'}.$$

The amounts of heat entering and leaving the working system in this cycle are therefore in the ratio of the absolute temperatures at which they enter and leave.

By simple transformations we may bring the last equation into the following forms:—

$$\frac{Q - Q'}{Q} = \frac{T - T'}{T} \text{ and } \frac{Q - Q'}{Q'} = \frac{T - T'}{T'}.$$

Now  $Q - Q'$  is the heat transformed into work; consequently the heat transformed into work is to the total communicated heat as the difference of the temperatures between which the process takes place is to the absolute temperature of the communication; and in the same way the transformed heat is to the heat leaving the system as the difference of temperature is to the temperature at which the heat leaves.

If only small differences of temperature are considered, the work which a quantity of heat can perform in a reversible cycle is inversely proportional to the absolute temperature at which the transformation takes place.

Were it possible to reach the absolute zero of temperature,  $T'$  in the equation  $\frac{Q - Q'}{Q} = \frac{T - T'}{T}$  would assume the value 0, and the right-hand side would become equal to unity. From this it follows that  $Q' = 0$ , *i.e.* if the lower temperature could be made the absolute zero, all the heat communicated would be transformed into work.

The quantity  $\frac{Q - Q'}{Q}$  is what we formerly termed the economic coefficient. As the reversible cycle above described is the most perfect imaginable, it follows that the economic coefficient or the efficiency of an engine can never be greater than  $\frac{T - T'}{T}$ . A steam-engine, for example, working with steam at  $150^\circ \text{ C.}$  and a condenser at  $17^\circ \text{ C.}$  can at most transform only  $\frac{150 - 17}{150 + 273} = \cdot 31$  or scarcely a third of the heat it receives into work. In practice the result is mostly much less favourable.

With the same final temperature we get greater efficiency as the initial

temperature rises. Between  $1000^{\circ}\text{C.}$  and  $0^{\circ}\text{C.}$  a perfect engine would transform as much as .785, or nearly four-fifths of the heat into work.

The principle that the transformable heat is inversely proportional to the absolute temperature has numerous important applications. Although higher mathematics is indispensable for their rigorous development, still a few of them may at least be indicated.

With the help of the principle we arrive at a very important relation respecting the vaporisation of liquids. Let us consider unit mass of a liquid whose volume is  $v_1$  and which is under the pressure  $p_1$ , equal to the pressure of its vapour; let the temperature be  $T$ . If we raise the temperature by a very little, say from  $T$  to  $T + dT$ , understanding by the symbol  $d$  that a very small fraction of the

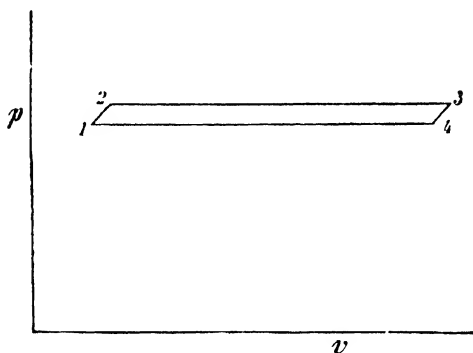


FIG. 51.

magnitude following is indicated, the volume increases by  $dv$  and the pressure by  $dp$ . Suppose the liquid to pass entirely into vapour. For this purpose we must communicate to it  $\rho$  units of heat,  $\rho$  being the latent heat of the vapour. The pressure during this time remains constant, and the volume increases very considerably; this increase, or the volume of the vapour

minus that of the liquid, we shall call  $u$ . Let now the vapour be again cooled through  $dT$ , and, at the temperature  $T$ , and the corresponding pressure  $p$ , be condensed to liquid until it returns finally to its initial state. The graphic representation of this cycle is given in Fig. 51, where the work obtained is represented by the quadrilateral 1 2 3 4.

The equation

$$\frac{Q - Q'}{Q} = \frac{T - T'}{T}$$

holds good, and  $Q - Q'$  being the heat transformed is equal to the work given by the quadrilateral 1 2 3 4. The area of this is equal to the product of the line 1 4, representing the difference of volume  $u$  on vaporisation, into the height, which is the increase of pressure  $dp$ ; consequently  $Q - Q' = u dp$ . The communicated heat  $Q$  is the latent heat  $\rho$  of the vapour. For  $T - T'$  we substitute  $dT$ , the difference of temperature of the two operations of the cycle, and therefore obtain

$$\frac{u dp}{\rho} = \frac{dT}{T}.$$

The equation is usually written in the form

$$\rho = T u \frac{dp}{dT}$$

and gives a relation between the heat of vaporisation, the increase of volume, and the rate of change of pressure with the temperature.\*

By means of this equation we can easily prove the statement made on p. 139 that the curves of vapour pressure for ice and water meet at a definite angle. For the vaporisation of ice we have a similar equation—

$$\rho' = Tu \frac{dp'}{dT}.$$

If from this we subtract the first equation, we get

$$\rho' - \rho = Tu \left( \frac{dp'}{dT} - \frac{dp}{dT} \right).$$

The magnitude  $dp'$  stands for the increase of the vapour pressure of ice brought about by the rise of temperature  $dT$ ;  $dp$  is the same value for water. The heat of vaporisation of ice  $\rho'$  is greater than that of water  $\rho$  by the heat of fusion of ice,  $\lambda$ , *i.e.*  $\rho' - \rho = \lambda$ . The curve for ice is thus  $\frac{\lambda}{uT}$  steeper than that for water, for the rate of increase of pressure is greater by this amount, and the corresponding curve must therefore below  $0^\circ$  C. have shorter ordinates than those for the (overcooled) water, as is graphically represented on p. 139.

Another conclusion which we may draw from the foregoing equation serves to connect the melting-point of ice with the pressure. We write the equation in the form

$$dT = \frac{Tu}{\rho} dp,$$

and have in  $dT$  the change undergone by the temperature of transformation owing to the change of pressure  $dp$ . If, as is the case for vapours, the magnitude  $u$ , or the volume in the second state minus the volume in the first, is a positive magnitude, then as  $T$  and  $\rho$  are also positive,  $dT$  and  $dp$  have the same sign—the pressure increases simultaneously with the temperature. When ice changes into water the volume is diminished;  $u$  is therefore negative, and  $dT$  and  $dp$  have different signs, *i.e.* by increasing the pressure we lower the melting-point. For other substances expanding on fusion, the melting-point rises with increasing pressure.

By introducing the proper numerical values we can calculate the change of temperature occasioned in the melting-point of ice by increasing the pressure one atmosphere.  $T = 273$ ,  $\rho = 80$  cal., or  $80 \times 42,350$  in gravitation units; the change of volume of 1 g. of ice on melting is  $u = .09$ , as

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\* The equation has been deduced for the passage of a liquid into vapour, but we can easily see that a perfectly similar formula can be obtained for every transformation from one state into another (heterogeneous) state, if the transformation takes place at a constant temperature and under constant pressure (*e.g.* ice into water, or calcium carbonate into calcium oxide and carbon dioxide).

1 g. of ice occupies 1.09 c.cm. ;  $dp = 1 \text{ atm.} = 1033 \text{ gravitation units.}$  We have thus

$$dT = \frac{273 \times 1.09 \times 1033}{80 \times 42350} = .0075^\circ.$$

It requires therefore 130 atm. pressure to lower the melting-point of ice 1 .

A specially interesting application of the equation is that to *chemical dissociation*. This is a process (see Book X.) which is in *complete formal correspondence with vaporisation*, a substance by heating undergoing a chemical decomposition which at a specified temperature continues till the product of decomposition evolved has reached a certain pressure, corresponding to the vapour pressure. In the equation,  $p$  then becomes the heat of dissociation or decomposition.

This may be calculated if we have ascertained the value of  $\frac{dp}{dT}$ , i.e. the alteration of the dissociation pressure with the temperature. As the latter may in many cases be measured where the former is directly inaccessible, we obtain in this way an important aid to assist us in penetrating into this difficult region.

# BOOK VIII

## PHOTOCHEMISTRY

### CHAPTER I

#### INTRODUCTORY

IN all the forms we have hitherto discussed, energy appears in intimate connection with matter, so that a given quantity of matter of definite properties contains a definite quantity of energy. Even where we have actions at a distance, as is the case with gravitation, the energy dependent on these is proportional to the quantity of matter and vanishes along with it.

All this is different with energy which is distributed by radiation. During the space of eight minutes, which the heat of the sun requires to reach the earth, the energy has no ponderable material vehicle, at least none whose mass is known to us. It is true that no circumstance goes to show that space is filled with energy; it seems rather to behave very nearly as a perfect void. Only when obstacles are put in the way does the existence of energy from its action make itself apparent.

The propagation of radiant energy is by no means instantaneous; it requires time, although very little. The speed is  $3 \times 10^{10}$  cm. per second. It appears, therefore, reasonable to attribute to the ether, the hypothetical vehicle of radiant energy, a mass extremely small, supposing its motion to take place according to the formula  $v = \sqrt{\frac{\epsilon}{m}}$ ,

where  $\epsilon$  is the elasticity and  $v$  the velocity of propagation.

The action exerted by radiant energy when it meets ponderable matter may be of many kinds; the radiant energy can transform itself into almost every other form. The transformation into heat is the easiest and most complete, but what interests us chiefly is the chemical action of radiant energy, an action which plays a most important part in the earth's economy.



It has been already emphasised that chemical energy is the main, almost the sole, source of our available energy. Energy is produced by chemical processes taking place in the sun, it is communicated to the earth by radiation, and there passes in the first instance into the form of heat, and indirectly into the mechanical energy of meteorological processes, seen in the movement of air and water. Another portion of the radiated energy, however, reassumes through the instrumentality of plants the permanent form of chemical energy.

Through the action of sunlight there takes place in plants a series of important chemical processes, the details of which are mostly unknown to us, but their result is that the carbonic acid of the atmosphere is decomposed into oxygen, which escapes, and compounds of carbon, in particular starch, which remain. As the heat of the combustion of starch into carbonic acid and water is 4123 cal. per gram, this amount of energy is necessary in order to form starch from the carbonic acid and water at the disposal of the plants, and is supplied entirely by the radiant energy from the sun, for without sunlight plants are unable to effect the reduction of the carbonic acid.

We see at once how this process affords us energy in a much more useful form than the meteorological processes, and in reality the portion supplied by the latter to drive windmills or water-wheels is very small compared to that stored up for us by the action of living plants. All fuel has this origin, and the animal organism can satisfy its requirements for energy in no other way than at the cost of the energy stored in the vegetable world.

Another and very important peculiarity of radiant energy is the extreme delicacy of its distribution in space. In striking contrast to the heat that clings to matter and is continually subjected to a process of obliteration or diffusion, radiant energy retains in the minutest particular all differences in position originally imparted to it, even after it has moved millions of miles through space.

On this property depends in the first instance our power of seeing, which, to use Herschel's phrase, endows us more than any other with the attribute of omnipresence. The numberless minute differences possessed by radiant energy when it leaves matter, generate in the retina corresponding chemical changes, which give us a more faithful and more complete conception of the external world than is given by any other sense. This same property has also acquired technical importance: in photography, processes of quite comparable character are excited on a plate sensitive to light, which render possible the permanent preservation of an exact record of momentary states and phenomena.

Photochemistry, then, like thermochemistry, was first developed round physiological and technical problems, the commencement in both cases being made about the same time. Priestley in 1772 made the observation that green plants in sunlight improve air vitiated by

breathing; Senebier and Ingenhousz thereupon recognised that the process consisted in a decomposition of carbonic acid and elimination of oxygen. The important part played by this in nature was, however, only sufficiently appreciated by Liebig (1840), and J. R. Mayer (1842).

The oldest observations on light-pictures obtained with silver chloride were made by J. H. Schultze (1727), but remained isolated. The power of different rays to exert different actions on a sensitive substance was recognised by Scheele (1777), who first photographed the spectrum. Ritter discovered in 1801 that the chemical action extends even beyond the visible spectrum. Wollaston then took advantage of the blackening of silver chloride to copy silhouettes. Photography proper commences with Daguerre (1838), who discovered the development of light-pictures, on which rests the possibility of retaining the pictures of the camera obscura, and of photography with great rapidity. The principle of it is that extremely feeble photochemical actions, themselves unable to effect any visible alteration on the sensitive surface, may afterwards have their effect rendered apparent by suitable treatment of the surface, and thus be converted into a picture. Although the means of arriving at this result have greatly changed since Daguerre's time, the principle still remains the same.

## CHAPTER II

### THE MEASUREMENT OF THE CHEMICAL ACTION OF LIGHT

As we have seen, Scheele's experiment proved the difference between the different rays of light with regard to their chemical action. As the majority of the substances first investigated are most strongly acted on by the blue, violet, and ultraviolet rays, the idea became prevalent that in the light-rays three distinct and independent kinds of wave-motion were contained, viz. radiant heat, light, and chemical radiation. This idea has proved to be utterly wrong, and our whole present knowledge of the subject shows that there is only one kind of radiant energy, which produces the different effects according to its rate of vibration and the nature of the object.

Chemically active light therefore being in no respect different from visible light, is subject to exactly the same laws as the latter. It may be reflected, refracted, polarised, etc. In a word, every optical phenomenon can be photographed—a proof that it is the light-rays themselves which produce photographic action.

The measurement of the chemical activity of light is an important and difficult task. In general it coincides with the measurement of any form of radiant energy, and is executed by means of thermoelectric or bolometric apparatus, for a description of which a text-book of physics should be consulted. We shall only sketch here the methods which are based on the quantitative determination of chemical processes. These methods, it is true, yield results which depend on the nature of the sensitive substance employed (for, according to the nature of the substances, rays of equal objective intensity but of different wavelength may have different actions); but still the general laws of photochemical action, as far as they are independent of the wavelength, may be established by means of such methods.

The formation of hydrogen chloride from a mixture of equal volumes of chlorine and hydrogen under the influence of light has found the most extensive application. After Draper (1843) had constructed a somewhat imperfect apparatus for this purpose, Bunsen

and Roscoe (1857) in a masterly research brought the method to the highest perfection.

The principal part of the apparatus is shown in Fig. 52. The mixture of chlorine and hydrogen prepared in exactly the right proportions by electrolysis is led from *h* through the "insulating" chamber *i*, which is made of thin glass

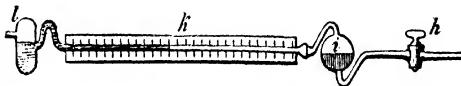


FIG. 52.

blown in the form of a flat circular box, and contains water in its blackened lower half. It is connected by a ground-glass joint with the measuring-tube *k*, which ends in the chamber *l*, also filled with water.

If light falls on the upper portion of *i*, hydrogen chloride is formed, and this is immediately absorbed by the water. A diminution of volume is the result, and the water *lk* in the tube moves towards *i*; the distance the water has moved is read off on the scale, and is a measure of the chemical action of the light.

Bunsen and Roscoe's apparatus is still at the present day the most perfect for scientific purposes, but its management is troublesome and difficult. Its originators themselves for ordinary purposes used another method, first employed by Senebier, which turns upon the blackening of paper coated with silver chloride. The amount of blackening cannot of course directly be given numerically, but a scale of blackness may be formed by allowing light, whose intensity can be easily regulated to any required degree by optical methods, to act on the paper, so that when a certain degree of blackness is produced on the paper by an unknown source of light we may approximately measure the intensity of the latter by comparing the darkening produced with the prepared papers of the scale.

A photochemical law which will be discussed later is here assumed, viz. that equal chemical effects are produced when the products of light-intensity and time of exposure are equal. By this we are freed from the necessity of observing during the same time in all cases, when with very feeble light there would be no appreciable blackening at all, while with a powerful light-source the blackening would be so deep that no comparison between the two could be instituted, and so no measurement made. Making use of this principle, we have as the simplest actinometer a piece of chloride of silver paper in a frame of neutral gray colour. The times are observed which elapse before the paper attains the same colour as the frame, and then the intensity of the chemical rays may be put inversely proportional to these times.

Other actinometers, of which many have been constructed, offer nothing essentially different from the two just described. Only one method, as yet not much used, contains a new principle. It is the galvanic measurement of photochemical action, and is due to Bec-

querel. Two silver plates coated with silver iodide are immersed in acidulated water or a solution of common salt contained in a glass trough and connected with a galvanometer. As soon as light falls upon one plate, the original symmetry of the arrangement ceases, and the galvanometer indicates a current proportional to the intensity of the light. Becquerel discovered and investigated quantitatively a number of important facts and laws of photochemical action with this apparatus. The method is capable of the greatest refinement and deserves much more attention than it has hitherto received.

Quite recently (1888) Gouy has described another arrangement also very sensitive. Two strips of copper—one bright, the other coated with cuprous oxide, by heating in the air—are immersed in a solution of ammonium or sodium chloride. Detailed investigations have not yet been published.

As already mentioned, attention must be paid to the fact that all actinometers are specifically different with respect to the nature of the rays to which they are exposed, *i.e.* they are influenced differently by light of different wave-lengths, depending on the nature of the sensitive substance.

## CHAPTER III

### LAWS OF PHOTOCHEMICAL ACTION

It follows from the fact that every objective optical phenomenon can be photographed, that the geometrical laws of light deduced under the assumption of rectilinear propagation hold unchanged for the chemically active portion of radiant energy. Special proofs of these laws are therefore of no particular importance.

The optical laws depending on the intensity of light are more difficult to investigate and require in part special methods. In the first place, it has to be found if the chemical activity is proportional to the intensity. This is a fundamental question for all photochemical measurements, and has been, in fact, assumed *à priori* to be self-evident.

An experimental proof of the principle was first given by Draper in 1842. He projected an image from a uniformly illuminated white surface by means of a large lens on his apparatus, which measured the action of light by the amount of hydrogen chloride formed from a mixture of chlorine and hydrogen. The result he obtained was, that when the lens was partially covered by sectors of known angle, the action was proportional to the uncovered surface of the lens. Hankel (1862) and Bunsen and Roscoe (1862) confirmed this law. It holds good only on the assumption that the experimental conditions during the process are not greatly altered,—in particular, that the chemical process does not suffer a change of velocity from the substances formed by the action.

If the chemical action, *i.e.* the quantity of the substance which has undergone chemical change, is proportional to the light intensity, and if the action proceeds uniformly, then, when the exposure has lasted a certain time, the total action is proportional to the product of the light intensity into the time, or, as it is called, to the “photochemical effect.”

The conditions just formulated being fulfilled, the principle follows from them as a necessary consequence. But even when the second condition is

not fulfilled, *i.e.* when the intensity of the action is altered by the change which the substance has already undergone, the same principle still holds in the special form, that for the attainment of the same amount of chemical action the products of light intensity and duration of action must have the same value. This may be proved mathematically, and was assumed to be self-evident by Senebier and Malaguti. Bunsen and Roscoe as well as Hankel have also tested it thoroughly from the experimental side, so that no doubt remains as to its general applicability.

Another law is the well-known one that the intensity of radiation from a point varies inversely as the square of the distance from that point. Bunsen and Roscoe confirmed this law for photochemical action by means of their hydrogen and chlorine actinometer; its validity has also been proved for the decomposition of carbonic acid in green plants.

A series of relations developed by Fresnel for the passage of light from one transparent medium into another were also tested by Bunsen and Roscoe and found in agreement with experiment. The enumeration of the various formulæ may be dispensed with.

If light passes through an absorbing medium, its intensity will decrease geometrically as the thickness of the medium increases arithmetically. This was also confirmed by Bunsen and Roscoe for photochemical action. The same experimenters proved that a coloured liquid diminishes the chemical action proportionally to the quantity of dissolved colouring matter, just as it does the optical intensity.

Whilst in all these laws we have only a confirmation of the facts obtained with purely optical phenomena, a new problem appears when we inquire into the quantity of energy spent in the chemical action. Bunsen and Roscoe obtained an answer in the following way.

A beam of light from a constant gas-jet was first passed through a cylinder filled with chlorine, and the loss by radiation to the chlorine measured. A cylinder of double the length and filled with a mixture of equal volumes of chlorine and hydrogen was then placed in the path of the beam. As hydrogen does not absorb radiation in any measurable degree, the light on passing through the mixture should have been weakened to the same extent as in the chlorine alone, if it performed no other work in the second case than it did in the first. The weakening, however, was found to be perceptibly greater, so that the authors came to the following conclusion:—

“Two-thirds of the rays of a gas-jet absorbed by the mixture of hydrogen and chlorine serve to heat the gases, while the remaining third is spent in performing the work necessary to put the two gases into such a condition that they can enter into chemical combination.”

Investigations into the active portion of light falling on a sensitive substance have shown that it is in general very small. According to Pfeffer 0.000,000,0537 g. of starch is formed by a square centimetre of surface of an oleander leaf per second. The heat of

combustion of this quantity is only  $\cdot 00022$  cal., which consequently is also the energy spent by light in forming the starch. Now the radiant energy received by a square centimetre on a clear summer day is  $\cdot 03$  cal. per second; the plant therefore cannot use as much as the hundredth part of this for chemical purposes.

From this circumstance we see why there is such a slight connection between the absorptive power of chemically active substances and the intensity of the action of the different rays. It cannot be doubted that only the rays that are absorbed exercise any chemical action, but as only a small proportion of the absorbed rays exert chemical action at all, the general optical absorption scarcely ever represents in any way the special chemical absorption. The latter is, to be sure, contained in the former, but is in general completely masked by it.

It has been several times stated that substances are affected differently by different rays. As a rule, rays of short wave-length are most capable of chemical activity, but just in the most important case—the decomposition of carbonic acid by green plants—it is the rays with greater wave-length, the red and yellow rays, which are the most active. The green-yellow rays act most intensely on the retina, in which the irritation resulting in the sensation of sight is probably also a chemical process.

On what circumstances these differences depend is as yet entirely unknown. Absorption plays a part, inasmuch as unabsorbed rays are necessarily inactive; but why certain absorbed rays exert chemical action, while others produce only a heating effect, is at present beyond our power of discernment.

A general hypothetical notion of the process of the chemical action of radiant energy can be obtained by taking into consideration the specific influence of the vibratory period of the latter. It is known that heated bodies radiate energy whose wave-length always decreases with rise of temperature. There take place therefore within the heated bodies processes that can produce such vibrations of the ether. Conversely, it seems conceivable that when the vibrating ether acts on ponderable bodies, it will generate within them states comparable to those they assume at a high temperature. This is only possible under quite special conditions, namely, when the vibrations excited by the ether in the body are of the same period as those of the ether itself. Only under this condition does a specific absorption take place, just as a string can take up the energy of vibration of a musical tone to any great extent only when it has the same period of vibration as the tone.

Through such an unusual excess of energy the molecules excited to vibration will behave differently from molecules in the ordinary state. A disturbance of the whole molecular structure will in general be produced, and if the atoms can assume more stable positions than



before, they will do so. Here we have the frequent case of decomposition by the action of light. It is, however, also conceivable that the excess of energy will be employed in rendering processes possible which are associated with consumption of energy; this is the case with the decomposition of carbonic acid in green plants.

The first action of light on sensitive substances is thus always the performance of work. The behaviour of a mixture of chlorine and hydrogen has often been compared to the explosion of gunpowder, the rôle of the spark being attributed to light, which would thus only loosen the combination. This is undoubtedly correct when the mixture is exploded, which, however, only happens when the light works so powerfully that by the combination of the first particles, the neighbouring particles are heated above the temperature of ignition, the action being in this way propagated with great rapidity through the whole mass. It is quite different with the apparatus of Bunsen and Roscoe: the heat is here conducted away as it is liberated, and the action does not go on. The fact that in this apparatus the amount of combination is proportional to the action of the light is a sure proof that the light in this case performs work proportional to its intensity; for the gaseous mixture is not an unstable substance in the proper sense. In dynamics, equilibrium is termed unstable when the smallest amount of work is sufficient to destroy it and effect a more or less important alteration in the system. The mixture of chlorine and hydrogen, however, may be warmed to a considerable extent without exploding, and mechanical disturbances have no effect on it. It is therefore evidently in a state of stable equilibrium. But its atoms can assume a still more stable state, namely, by forming hydrogen chloride.

A dynamical comparison may be found in the equilibrium of a prism standing on its end. The equilibrium is stable, for small disturbances are insufficient to overturn it. If the displacement, however, exceeds a certain amount, quite definitely specified by the nature of the prism, it falls over. This work is to be compared to the work done by light in the gaseous mixture, and the quantity of hydrogen chloride formed is proportional to the intensity of the light, *i.e.* to the available work.

## CHAPTER IV

### PHOTOGRAPHY

THE method by which Daguerre first accomplished actual photography consists in exposing a plate of silver (or of thickly silvered copper) to the vapours of iodine, and then allowing the image in the camera obscura to act on the plate. After the action, which only requires a few minutes, the plate, on which no image is visible, is exposed to the vapours of gently heated mercury. The vapours condense on the plate the more densely, the more strongly the light has acted at the spot in question. If the plate is looked at so that the bright places reflect little light to the eye, the parts where there is a deposit of mercury globules appear brighter than the background, proportionately to the thickness of the deposit.

The theory of this process is based on the fact that vapours condense in general more readily on rough than on smooth surfaces. Where the silver iodide has been acted upon by light it is partially decomposed, and thus a better surface is offered for the deposition of the mercury globules. We may perhaps have the circumstance in addition that the separated silver has more affinity for the mercury than the undecomposed iodide has, and therefore condenses it more readily. From the researches undertaken after the acquirement of the knowledge of Daguerre's method, it has been proved that the slightest local alteration in the state of the surface of a polished sheet changes the manner in which vapours condense on it in the most remarkable way.

Daguerre's method is now completely abandoned. It was first displaced by Scott Archer's collodion process. A solution of gun-cotton (cellulose nitrate) in ether and alcohol is made to dissolve certain iodine compounds (cadmium iodide, ammonium iodide, etc.) A glass plate is then coated with the solution, and after the greater part of the ether has evaporated, dipped into a solution of silver nitrate. By this means a sensitive precipitate of silver iodide is formed in the coating of collodion. If such a plate is now brought into the camera and exposed for the necessary length of time—a few seconds in daylight—no alteration in the yellowish-white coating is observed. An image

only appears when the plate is immersed in a mixture of silver nitrate and a reducing liquid, *e.g.* a solution of pyrogallol or of ferrous sulphate. The silver which separates from this mixture deposits preferably on the places where the light has acted, and produces an image in which the silver deposit is proportional to the light-intensity. By treating this "developed" image with a solvent for silver iodide, *e.g.* potassium cyanide or sodium thiosulphate, the excess of iodide is removed and we have left a negative, with the light places transparent and the dark places opaque.

As the foundation of the theory of this process we have the circumstance that solid substances which are deposited from liquids collect preferably at parts where some of the solid is already present (cf. p. 146). By the action of light minute traces of silver have been formed, and each silver particle acts as a centre of attraction for the silver of the solution, so that this is distributed proportionally to the number of these centres. The process can be prolonged until the thickness of the deposit is sufficient for the required purpose, but for the reasons just explained the grain of the photograph gets coarser as the development is continued.

The collodion process also is now almost entirely given up. The plates prepared as above must be used wet as they come out of the silver bath, so that they can only be made ready shortly before the taking of the photograph. The plates at present in use, on the other hand, can be prepared an indefinitely long time before use. They are made by pouring a solution of gelatine, in which precipitated silver bromide is suspended, with certain precautions, on glass plates and allowing it to dry. These "gelatino-bromide" plates are much more sensitive to light than the "collodio-iodide" plates. Like the latter, however, they show no image after exposure, but must be developed. For this purpose we do not use a solution from which silver is precipitated, but a strong reducing agent alone, such as potassium ferrous oxalate or an alkaline solution of hydroquinone. The development consists in the reduction of silver bromide to silver on the exposed parts.

The theory is similar to the theory of the collodion process. Here also the silver slowly produced by the action of the reducing agent on the bromide is deposited first on those places which are in the neighbourhood of the silver particles liberated by the light. Or, as we may perhaps more accurately put it, the particles of silver bromide that lie near metallic silver are rendered more easily reducible by this circumstance. This may be seen by placing an unexposed gelatine plate in the developer and touching it at one point with a silver wire; a black speck of reduced silver is immediately formed.

All these methods give only negatives. The positive photographs are obtained by a copying or printing process, light being allowed to fall through the negative on a prepared sensitive paper against which the negative is pressed; the light and shade are now reversed and appear in the proper order.

The number of copying processes is very great. Silver compounds which blacken in the light are usually employed, paper coated with albumen, "salted" with ammonium chloride, and afterwards sensitised in a silver nitrate bath being in very general use. A number of other processes are founded on the fact that a mixture of gelatine and a salt of chromic acid becomes insoluble on exposure to light, the acid being reduced to chromic oxide, which yields an insoluble compound with the gelatine. We have other methods depending on the reduction by light of ferric salts in the presence of organic substances, such as oxalic acid, tartaric acid, sugar, and the like. Facts of general interest are here scarcely to be recorded.

A remarkable observation was made in 1874 by H. W. Vogel. As we have already had occasion to mention, silver salts are usually specially sensitive for rays of small wave-length—blue, violet, and ultraviolet. If sensitive plates (especially gelatino-bromide plates) are dyed with different organic colouring matters, the region of sensibility is more or less changed; it is displaced in particular to the side of greater wave-lengths. The action has not yet been fully explained; although it is manifest that only such rays as are absorbed can act, and that by employing suitable colouring matters the corresponding rays are absorbed in the plate, still we cannot see how the action of the rays absorbed by the colouring matter is transferred to the neighbouring particles of silver bromide, so that a sufficient explanation of this observation of both great theoretical and practical importance is left to the future.

# BOOK IX

## ELECTROCHEMISTRY

### CHAPTER I

#### INTRODUCTORY

A ROD of perfectly pure zinc is not attacked by dilute sulphuric acid, neither is a rod of platinum. But if we immerse simultaneously a zinc rod and a platinum rod in the acid and bring the projecting ends into contact, either directly or by means of a metallic wire, the zinc is dissolved, and the hydrogen expelled from the acid appears on the platinum. The connecting wire has at the same time assumed peculiar properties; if a magnetic needle is held parallel to it, the needle suffers immediate deflection; if it be cut at any point and the ends placed apart from each other on a piece of litmus paper moistened with a solution of salt, there appears at the end connected with the zinc a blue speck, and at the end connected with the platinum a red speck; lastly, the wire becomes warm. All these phenomena cease on the removal of one of the metals from the liquid.

They serve to show that with the arrangement described, the chemical action between zinc and sulphuric acid produces effects at a distance from where it actually takes place, in the wire, namely. The chemical energy produced where the acid attacks the zinc must therefore have been transformed into another form capable of passing through metals and liquids, and of exercising chemical and thermal actions at any part of its course.

The only change to be observed in the properties of the substances taking part in the action is that the metals have become charged with electricity, the charge on the zinc being negative and on the platinum positive. If the two metals be connected by a conductor the difference is not adjusted, for after the removal of the conductor the metals are again found to be charged. But we know that opposite electrical

charges in metallic conductors neutralise each other. It only remains therefore to conclude that the charges are continually neutralised by means of the connecting wire, but that they are just as regularly reproduced in the metals. By this process there comes into existence in the system what is termed an electric current. The electric current is connected with the chemical action on the zinc, not only in point of time, but also casually. The current ceases when the chemical process is in any way prevented: it can perform work, and consequently contains energy, which it must derive from the chemical process, this being the only available source. We may thus say that, in the system we have described, chemical energy is transformed into electrical energy.

The transformation must, in the first instance, be subject to the law of the equivalence of energy. Since, during the solution of zinc in sulphuric acid as usually performed, all the chemical energy is transformed into heat, so much less heat must appear at the seat of reaction, the more electrical energy passes into the connecting wire. If this also is changed into heat, the sum of all the different quantities of heat produced must be constant, and equal to the heat of solution of the zinc.

These consequences of the fundamental principle of energy have been experimentally tested by Joule and especially by Favre (1854) and confirmed in all particulars. From a system consisting of zinc, sulphuric acid, and platinum—a galvanic (or voltaic) element as it is usually called—more than half the heat of solution of the zinc may be obtained in the form of electrical energy; but if this be again changed into heat by conducting the current through a long thin wire, the original quantity of heat is exactly reproduced.

By making use of the electromagnetic forces we can transform the electrical energy, obtained from the chemical, into work. The total evolution of heat in this case is smaller by the thermal equivalent of the mechanical work done. This result was also confirmed by Favre.

Lastly, we can use the electrical energy to perform chemical work. If the current from several such galvanic elements is conducted to two platinum plates immersed in dilute sulphuric acid, a development of oxygen and hydrogen on these takes place. The total heat given out is again less than before, and that exactly by the amount of the heat of combination of the two gases to form water. Here once more we have strict fulfilment of the law of the conservation of energy.

Like the other forms of energy, electrical energy appears as the product of two factors, one of which is called the quantity of electricity, the other—potential, tension, or electromotive-force. The first factor is a quantity, the second an intensity, so that electrical energy capable of unrestrained movement in a system can only assume a permanent stable state when the second magnitude is

the same throughout the system. When this is not the case, a change of state occurs from which work may be obtained, just as it can be got from a change of state of heat or of any other form of energy.

The other factor, the quantity of electricity, is usually looked upon as being the real existent thing that lies at the bottom of all electrical phenomena, and the whole nomenclature of electrical science has been formed in correspondence with this conception. Although the view has often been found very convenient, it must still be borne in mind that the thing underlying electrical phenomena is electrical energy, and that the nomenclature usually adopted is only of value as affording us, in many cases, a means of clear and concise formulation.

If the quantity of electricity in a galvanic current passing through a section of the conductor in one second be denoted by  $I$ , intensity; and the electromotive-force between two parts of the circuit by  $E$ ; then, by definition, the energy corresponding to this motion of electricity is  $EI$ . If the current in the part of the circuit considered performs no external work, its energy is completely transformed into heat; if we denote this by  $H$ , we get

$$H = EI.$$

We are accustomed to conceive the way in which electrical energy passes into heat as being analogous to the conversion of the mechanical work of a flowing liquid into heat—a sort of friction is supposed to resist the motion of the electricity, and the operation of overcoming this conditions the transformation of the electrical energy into heat. The electromotive-force corresponds to the pressure under which the liquid moves. We therefore define the resistance  $R$  of a conductor in accordance with these ideas, as the quotient of the electromotive-force  $E$ , by the quantity of electricity forced by it through the conductor in unit time, *i.e.* by the intensity  $I$ . We have thus

$$R = \frac{E}{I} \text{ or } I = \frac{E}{R}.$$

This is the well-known law of Ohm, that the intensity or current-strength is equal to the electromotive-force divided by the resistance.

If in the equation  $H = EI$  we substitute for  $E$  the equivalent value  $RI$  it follows that

$$H = RI^2.$$

The quantity of heat developed by the passage of electricity through a conductor is proportional to the square of the intensity (the quantity of electricity passing per second) if the resistance is constant, and proportional to the resistance if the intensity is constant. This law was experimentally discovered by Joule (1841) and has frequently received confirmation.

For the magnitudes above defined units have been introduced, which, in a manner that cannot be explained here, have been derived

from the consideration of electrostatic and electromagnetic processes. As unit of resistance we take that at  $0^\circ$  of a column of mercury 106 cm. long, and 1 sq. mm. in section; this resistance is called an ohm. The unit of electromotive-force, the volt, is so determined that the electromotive-force of a galvanic element composed of copper in a solution of copper sulphate and zinc in a solution of zinc sulphate, amounts to 1.10. These two units specify the unit quantity by the equation  $I = \frac{E}{R}$ ; it is that quantity of electricity which in one second

flows through the section of a conductor between the ends of which there is an electromotive-force of one volt, and the resistance of which is one ohm. This unit is called a coulomb, and the corresponding current-strength an ampère.

These magnitudes are so chosen that the electrical energy volt  $\times$  coulomb is equal to 10,000,000 absolute units. Now a calorie is equal to 42,350 gravitation units, or (as the intensity of gravity is 980 absolute units)  $42,350 \times 980 = 41,503,000$  absolute units. The unit of electrical energy, volt  $\times$  coulomb, is therefore equal to .241 cal., or a current of one volt electromotive-force passing for a second through a resistance of 1 ohm, 1 coulomb being thereby set in motion, develops sufficient heat to raise 1 g. of water from  $0^\circ$  to  $0.241^\circ$ .



## CHAPTER II

### FARADAY'S LAW

THE motion of electricity in bodies which admit of it at all takes place in two distinct ways. When electricity passes through conductors of the first class, these only experience heating according to Joule's law (p. 268), and no other material change. Metals, alloys, carbon, and a few other substances constitute this class.

Conductors of the second class can only permit the movement of electricity in such a way that a chemical change takes place in them simultaneously. The chief members of this class are salts, fused or in solution, and further, aqueous solutions of acids and bases—all of these being compound substances, as we see.

In such conductors of the second class, or electrolytes, the movement of electricity takes place so that the metals (or metallic radicals) of the salts and bases, and the hydrogen of the acids, move from the positive part of the circuit to the negative, while the acid radicals or elements, such as chlorine, bromine, iodine, and also the hydroxyl of bases, move in the opposite direction. These components, the ions, are set free where the electrolyte is in contact with metal conducting the current.

Faraday in 1833 discovered the general law that equal quantities of electricity on passing through different electrolytes require equivalent quantities of the ions for their transport. If several different electrolytes are introduced into the same circuit (in which according to the laws of electricity equal quantities of electricity pass through every section in equal times), then the quantities of the liberated metals or hydrogen, as well as those of the acid radicals, are in equivalent proportions.

We know that the equivalent of an element is its atomic weight divided by its valency. If we have, for example, solutions of silver nitrate, cupric sulphate, and antimony trichloride in a series in the same circuit, the quantities of metal simultaneously deposited are in the proportion of 108 of silver to  $\frac{1}{2}$  63.3 of copper to  $\frac{1}{3}$  120 of antimony. Of the acid radicals we obtain at the same time,  $\text{NO}_3$ ,  $\frac{1}{2}$   $\text{SO}_4$ , and  $\frac{1}{3}$   $\text{Cl}_3$ .

The electrolytic submolecules of equal valency behave as if each had the same capacity for electricity, so that equal quantities of electricity are conveyed by the same number of them, no matter what their nature.

We know that there are certain substances, especially metals, which can act with different valencies; thus, for example, mercury and copper are univalent and bivalent, tin bivalent and quadrivalent, iron bivalent and trivalent. According as one or other set of these compounds is used for conducting the current, each atom transports so many times the electricity capable of being transported by a univalent atom as the metal has active valencies in the compound in question.

If we take the electricity transported by one gram of hydrogen as our unit, 63.3 g. of copper in cuprous compounds convey one unit, and the same quantity in cupric compounds two units. In a similar way, 56 g. of iron in ferrous compounds transport two units, and in ferric compounds three units. The group  $\text{Fe}(\text{CN})_6$  as a component of potassium ferrocyanide transports four units of (negative) electricity; but in potassium ferricyanide only three. Having regard to this property we shall continually distinguish between univalent, bivalent, trivalent, etc., ions. Hydrogen and the metals, which convey positive electricity, are called positive ions or cations; the halogens and other acid radicals, by means of which the negative electricity is transported, are called negative ions or anions.

In order to understand Faraday's Law we must carefully guard against the error of supposing the separation of the ions at the electrodes, *i.e.* the places where the electricity passes from the electrolyte into the metallic portion of the circuit, to be the essential part of the law. That is not the case; the law refers rather to every kind of motion of the electricity within conductors of the second class. Of course the separation of the ions at the electrodes is the most convenient means of proving the accuracy of Faraday's Law, and as far as this proof has yet been taken the law holds strictly true; the quantity of electricity is always exactly proportional to the amount of the ions separated, and the latter are always in the ratio of their equivalents for equal quantities of electricity. In particular, not the slightest indication has been obtained of metallic conduction, which some physicists think possible, *i.e.* conduction of electricity independent of motion of the ions.

As Faraday's Law holds good for all movements of electricity within electrolytes, the development of electricity in galvanic elements (p. 267) must also be determined by it. If the ions of sulphuric acid in the system [zinc, dilute sulphuric acid, platinum] move so that the group  $\text{SO}_4$  goes towards the zinc and forms zinc sulphate with it, while  $\text{H}_2$  moves towards the platinum and is evolved there as gas, then two units of electricity as above defined must be set in motion for every 65.4 g. of zinc dissolved, or 98 g. of sulphuric acid decomposed. We may say in general that every galvanic element,

independent of its nature or of the character of the chemical process, produces the same quantity of electricity by consuming one equivalent of the metal.

It is of interest for many purposes to know the quantity of electricity moving with 1 g. of hydrogen or with the equivalent quantity of another ion. According to the experiments of Kohlrausch and Lord Rayleigh this amount is 96,540 coulombs. Conversely, a coulomb requires for its transport in an electrolyte  $\cdot 00001036$  gram-equivalents of any ion.

This consequence from Faraday's Law, that every galvanic element on the consumption of one gram-equivalent of its active substances always sets 96,540 coulombs in motion was extensively confirmed by Renault (1867). There appeared in particular numerous examples of a metal having different electrochemical equivalents, always in rational proportions, according to the nature of the compounds containing it. Thus 96,540 coul. are set in motion by 200 g. of mercury dissolving in dilute nitric acid to form mercurous nitrate, but 100 g. are sufficient when the solvent is potassium cyanide, mercuric cyanide,  $\text{Hg}(\text{CN})_2$ , being formed. The electrochemical equivalent of copper in dilute hydrochloric acid is 63.3, cuprous chloride being the product, while in dilute nitric acid it is 31.7, for then cupric nitrate is formed. Tin usually acts with the equivalent  $\frac{1}{2}$  118; but in potassium pentasulphide, when it dissolves with formation of  $\text{SnS}_2$ , its equivalent is only  $\frac{1}{4}$  118. Tellurium in hydrochloric acid has the equivalent  $\frac{1}{2}$  125, in potash  $\frac{1}{4}$  125.

Faraday's Law both in this form and in that respecting electrolysis was formerly misunderstood as meaning that equal quantities of electricity in the various equivalents conditioned the same expenditure or gain of work; Berzelius in particular was a violent opponent of the law owing to this misunderstanding. From our point of view we see that there is no question of energy or work here at all. Faraday's Law only considers one factor of electrical energy, viz. quantity; the other factor, electromotive-force, remains unheeded.

## CHAPTER III

### THE CONSTITUTION OF ELECTROLYTES

WE have already learned that by no means all compound substances are capable of conducting electricity electrolytically, *i.e.* by help of ponderable particles. The property is possessed principally by aqueous solutions of salts, acids, and bases; it is only observed with those substances that can instantaneously effect an exchange of their components.

If we think for a moment that for the purpose of electrolytic conduction particles laden with positive electricity must move in one direction, while particles charged with negative electricity move in the other, we see that the ability to conduct depends on the ability to form such vehicles for the electricity. Now no body existing in the molecular state is capable of being charged in such a way with positive or negative electricity; the property falls exclusively to the ions—the products of dissociation of the compounds mentioned.

Formerly, therefore, electricity had ascribed to it the property of effecting this decomposition on its entrance into an electrolyte, and of availing itself of the fragments for its own transport. Several facts, however, are at variance with this view. A certain amount of work would evidently be required to effect such a decomposition, but electricity according to our experience moves in electrolytic conductors with the same freedom as in metals; there is consequently no place for such work. Clausius therefore (1857) assumed, in unconscious agreement with an idea developed by Williamson (1851) for quite other purposes, that some of the molecules in electrolytes are decomposed in consequence of their collision; the parts, already separated, are immediately seized on by the electricity to effect its transport, so that it has to perform no work in the matter at all.

The question soon arises as to the proportion of decomposed molecules in a definite electrolyte, *e.g.* in a normal solution of potassium chloride (74.5 g. per litre). Clausius left this question unanswered and only stated his general opinion that the number was not necessarily large. Now, however, we can come to a decision by making use of

the laws regulating the influence of dissolved substances on osmotic pressure, vapour-pressure, and the freezing-point (pp. 127-143). An aqueous solution containing one gram-molecular-weight of sugar or any other indifferent substance dissolved in a kilogram of water solidifies at  $-1.89^{\circ}$ . If the corresponding solution of potassium chloride contains for the most part undecomposed molecules, it should have the same point of solidification. Actual observation, however, shows that the point of solidification is at  $-3.5^{\circ}$ , *i.e.* the depression is almost twice as great as for sugar, etc. From this it follows that there must be in the solution of potassium chloride almost twice as many molecules as would be calculated on the assumption that essentially molecules of the formula  $\text{KCl}$  existed there, and so the conclusion is forced upon us that almost all the potassium chloride has split up into its ions  $\text{K}$  and  $\text{Cl}$ . In harmony with this conclusion there is the fact that the other properties of the solution of potassium chloride (or in general of the solutions of electrolytes) exhibit quite similar abnormalities, so that the numerical values of the osmotic pressure and of the depression of the freezing-point lead to exactly the same conclusion.

We thus arrive at the result that solutions of salts and of strong acids and bases contain these substances only to a small extent as such, by far the greater part being dissociated into ions. This conclusion was first drawn by Arrhenius (1887), and although it conflicts with some of the views usually adopted, yet it is in complete agreement with a very great number of observed facts.

\* For example, the objection has been raised, that substances like potassium chloride, potash, or sulphuric acid are known to be compounds whose components have the greatest affinity for each other; but here the two conceptions of chemical affinity—stability on the one hand, and activity on the other—have been confused. Hydrochloric acid exchanges its hydrogen for metals, potash its hydroxyl for acid radicals with the utmost readiness; it would be absurd to ascribe to their components great affinity in the sense of firmness of chemical union—the very opposite is the case. Conversely we must say that the hydrogen in methane has great affinity for the carbon to which it is bound, for very energetic means are required to effect its separation. Thus it is the chemically inactive bodies that are held together by the most powerful affinity; compounds which react with ease and rapidity can only hold their components loosely bound, if bound at all.

Now, as we have already seen, electrolytes are precisely the most active substances. The connection between the two properties is very intimate, so close, in fact, that from the chemical activity we can determine the electric conductivity and *vice versa*. In accordance therefore with the idea of Williamson and Clausius, there is very little coherence between the ions of electrolytes.

To those not familiar with this mode of viewing the subject, it may appear somewhat strange that in a solution of potassium chloride there

should exist free potassium and free chlorine, as none of the properties of these free elements as we know them are apparent. Such an objection, however, would again rest on a misunderstanding. What actually exists in the solution is single potassium atoms with enormous electrical charges. We do not know what these charges are in reality, but this we know—that the chemical properties of substances are greatly altered by electrical charges. On the other hand, what we know as “free potassium” is a solid substance whose molecules consist of an unknown and probably great number of potassium atoms not charged with electricity at all. Similarity in the properties of an element in states so different is scarcely to be expected. As soon as the potassium atoms in solution lose their charge, as they do, for example, when led by an electric current to a platinum wire, where they can give up their electricity, potassium with its ordinary properties is at once produced, as is seen in its ability to decompose water with evolution of hydrogen.

Quite similar remarks apply to negative ions, *e.g.* to chlorine.

The following consideration may serve to remove the last doubts as to the validity of the assumption of free electrically charged atoms of chlorine and potassium. Imagine two insulated vessels A and B (Fig. 53) filled with a solution of potassium chloride, and electrically connected by means of the siphon H. Let a negatively charged body be brought near A; remove the siphon, and lastly the charged body K. Then, as is well known, A remains positively electrified, and B negatively electrified.

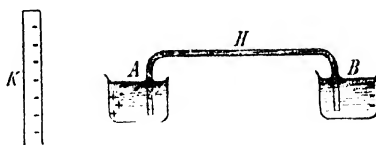


FIG. 53.

Now, according to Faraday's Law, the electricity in electrolytes can only move simultaneously with the ions. Consequently, if an excess of positive electricity is present in A, there must also be there an excess of free positive ions, *i.e.* of potassium atoms, by the electricity of which the charge is determined. If the electricity is conducted away, the potassium assumes the ordinary form, and acting on the water of the solution develops hydrogen, which can be collected in suitable apparatus and tested.

Similar considerations hold good for the chlorine in the vessel B.

It is consequently not only conceivable that the ions in an electrolytic solution move about with electric charges, otherwise quite free, but solutions may be prepared which contain an excess of any ion we choose, *e.g.* an excess of potassium. The assumption that electrolytes contain free ions is not only possible, but necessary.

Quite a number of phenomena, which were formerly unintelligible, have received their explanation from the theory of free ions. First of all we have Hess's Law of Thermoneutrality. Two neutral salts when mixed in aqueous solution produce in general no thermal change. This is because there is also no chemical change. A solution of

potassium chloride consists essentially of the ions K and Cl, one of sodium nitrate of the ions Na and  $\text{NO}_3$ ; when the two solutions are mixed the ions remain free as before.

Here we have an answer to the old question, Which salts are really in the solution? No salts are in the solution. The ions present, however, can form any of the salts according to circumstances, if that salt is capable of separating out of the solution, *e.g.* by crystallising. Thus it is explained why a mixture of solutions of common salt and magnesium sulphate can be separated into these components if the solution is evaporated down by heating (the sodium chloride being then the least soluble), but resolves itself if the evaporation takes place at the ordinary temperature into sodium sulphate, which is deposited (being at that temperature the least soluble), and magnesium chloride which remains in solution.

We must bear in mind, however, that these explanations only hold in strictness for very dilute solutions. When the solutions are concentrated, exceptions appear just as they do in strongly compressed gases, which no longer exactly follow the laws of Boyle and of Gay-Lussac. Such exceptions nevertheless do not obscure the fundamental principles.

The change of volume on neutralisation is also susceptible of a like explanation. It was seen from the consideration of the observed facts (p. 143) that the two components of the salts in their aqueous solutions led a comparatively independent existence. The theory of electrolytic dissociation gives a rational explanation of this result.

A whole series of other phenomena in salt-solutions—the refractive equivalents, constants of capillarity, specific heats, etc., can all be placed in the same category. Since, however, we have not before entered into the discussion of these relations on account of their relative unimportance, this mere indication may suffice here also.

In conclusion, the purely chemical facts distinctly favour the theory of the independent existence of the ions in electrolytic solutions. We have in analytical chemistry a large number of general reactions, which allow of the recognition of definite substances in their various compounds. Silver nitrate, for example, is a reagent for chlorine; all the metallic chlorides and similar compounds give a precipitate of silver chloride. But this is not the case with all chlorine compounds; the presence of chlorine in potassium chlorate or in monochloroacetic acid is not indicated by silver nitrate at all. Iron compounds give with ammonium sulphide a black precipitate of iron sulphide: but the iron in potassium ferrocyanide remains quite unaffected in the presence of ammonium sulphide.

When we look at these “exceptions” more closely, we see that only those compounds have the above-mentioned reactions, in which the substance sought for is contained as an ion. A solution of silver is thus not a reagent for chlorine compounds in general, but

only a reagent for the ion chlorine ; in potassium chlorate the ions are K and  $\text{ClO}_3$ , in monochloroacetic acid H and  $\text{CH}_2\text{Cl} \cdot \text{CO}_2$ , so that these compounds which contain chlorine, not as a separate ion, but only as a component of a more complex ion, show no chlorine reaction.

Indeed, analytical chemistry is in a great measure based on the exchange of ions. We have no reagents for this or that element, but only for definite radicals of salts or similar compounds. The numerous oxygen acids of sulphur, although they all contain the same elements, possess the most diverse reactions.

Further, the elements or radicals that appear as ions react differently according as they have a greater or less valency, *i.e.* are charged with more or less electricity. In the ferrous compounds where iron is bivalent, it exhibits quite other properties than in compounds where it is trivalent. The group  $\text{Fe}(\text{CN})_6$  as the ion of potassium ferrocyanide acts quite differently from what it does as the ion of potassium ferricyanide, although it has exactly the same composition whether it comes from the compound  $\text{K}_4\text{Fe}(\text{CN})_6$  or from  $\text{K}_3\text{Fe}(\text{CN})_6$ .\* In the first case, however, it conveys four units of electricity, in the second only three (p. 271).

These considerations might be greatly extended, but as the necessary facts are generally known, the application of the new electrochemical theory of saline compounds may be left to the reader.

\* The formula  $\text{K}_6\text{Fe}_2(\text{CN})_{12}$  used in many text-books for potassium ferricyanide has no foundation in fact ; recent investigations have all gone to prove the correctness of the simpler formula.



## CHAPTER IV

### THE ELECTRIC CONDUCTIVITY OF ELECTROLYTES

THE variations from the simple laws governing dilute solutions that are shown by aqueous solutions of salts, and which can be represented by the formula  $M = iM_w$  (p. 141), put us at once in a position to measure the extent of the dissociation into their ions of the molecules in electrolytic solutions. The factor  $i$  gives the ratio of the molecules actually present in the solution to the number calculated from the chemical formula of the substance. If we have thus an electrolytic substance, each molecule of which can split up into  $n$  electrolytic submolecules or ions, and if  $x$  represent the fraction of the molecules which have undergone the dissociation, then the relation  $i = 1 - x + nx$  or  $i = 1 + (n - 1)x$  is evidently true. For, if  $N$  be the total number of the original molecules, the solution will contain  $xN$  decomposed and  $(1 - x)N$  undecomposed molecules; but as, according to our assumption,  $n$  submolecules are produced from every decomposed molecule, the total number of molecules present will be  $(1 - x)N + nxN$ , and the ratio of this total to the number of original molecules is what we have represented above by  $i$ .

The number  $n$  depends on the constitution of the electrolyte. In a salt of the type of potassium chloride, in which a univalent metal is united to a univalent halogen or acid radical,  $n$  is equal to 2 because every  $KCl$  splits up into  $K$  and  $Cl$ . In sulphuric acid  $H_2SO_4$ , potassium sulphate  $K_2SO_4$ , or barium hydroxide  $Ba(OH)_2$ , we have  $n = 3$ , in potassium ferrocyanide  $K_4Fe(CN)_6$ , which decomposes into  $4K$  and  $Fe(CN)_6$  we have  $n = 5$ ; in barium ferrocyanide, on the other hand,  $n = 3$ ; aluminium sulphate,  $Al_2(SO_4)_3$  has  $n = 5$ ; and so on. It is to be noted that in the case of several polybasic acids the value of  $n$  does not correspond to the number of replaceable hydrogen atoms. Phosphoric acid  $H_3PO_4$ , for example, in moderately dilute solutions, only splits up into the ions  $H$  and  $H_2PO_4$  and has therefore  $n = 2$ . Such abnormalities will be explained later.

A far more productive means of learning the condition of dissolved substances is provided by the determination of the electric conduc-

tivity of their solution ; for the quantity of electricity passing through an electrolytic liquid is *ceteris paribus* proportional to the number of conducting, *i.e.* dissociated, molecules.

To arrive at a clear idea of the relations here involved, we may imagine a vessel formed of two electrodes of great extent, 1 cm. distant from each other, and the necessary non-conducting walls. Let so much of the electrolytic liquid be introduced into this vessel that it contains a molecular weight of the electrolyte in grams. This system will have a definite resistance (in ohms or mercury-units) and a corresponding conductivity ; these are called the molecular resistance and the molecular conductivity.

The molecular conductivity of a given electrolyte depends in the first instance on the temperature, increasing almost without exception with rise of temperature, and mostly by about 2 per cent per degree. It is further dependent on the state of dilution, increasing almost always simultaneously with this. The increase is very considerable for bad conductors, small for good conductors, the molecular conductivity everywhere approximating with increase of dilution to a limiting value which can be practically attained by good conductors ; in the case of bad conductors, even at the extremest dilutions accessible to measurement, the molecular conductivity is still far removed from limit.

The measurement of the electric conductivity of electrolytes was for a long time a very difficult operation ; a method at once convenient and exact was first given by Kohlrausch (1880). Such measurements are almost inseparably bound to the use of electrodes which, as soon as the current passes from them into the electrolytic liquid, become through "polarisation" the seat of unknown electromotive-forces (*vide infra*), so that the usual methods for conductors of the first class are not applicable here at all. By substituting alternating currents (*i.e.* currents that incessantly change their direction) for ordinary currents, Kohlrausch succeeded in obviating the disturbing influence of polarisation, and in rendering exact measurement possible. His apparatus is constructed on the plan of Wheatstone's bridge, and is diagrammatically represented in Fig. 54.

The alternating currents of a small induction-coil J are conducted to the ends a and b of a platinum wire 1 metre long and stretched on a scale divided into millimetres.

On the one hand they pass through the wire adb, and on the other through the resistance-box R and the conducting liquid W by the path aRcWb. From c a connecting wire passes to d on the platinum wire ab, and can be

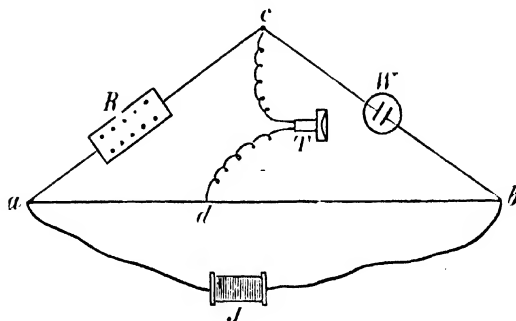


FIG. 54.

moved along in metallic contact with the latter by means of a small sliding carriage; in this branch the telephone T is introduced.

It is well known that in such an arrangement no current flows through the "bridge" *cd* when the resistance *R* is to the resistance *W* as *ad* : *db*. The silence of the telephone indicates when this occurs. We therefore move the carriage with *d* along the wire *ab* until we find the spot at which the telephone no longer speaks. As  $R : W = ad : db$ , the resistance *W* required is equal to  $R \frac{db}{ad}$ , or the conductivity  $L = \frac{1}{W} = \frac{ad}{R \cdot db}$ .

To calculate the molecular conductivity from the conductivity so obtained for the liquid in *W*, we must multiply the latter by the "capacity" of the resistance-cell, and also by the dilution, *i.e.* the number of litres in which a gram-molecular-weight of the electrolyte is contained. The capacity is found by introducing into the cell a liquid of known conductivity and composition, and finding its resistance. If *M* is the molecular conductivity of the liquid, and *V* its dilution, then we obtain the factor *K* for transforming the conductivity measured in the cell into molecular conductivity from the equation

$$M = K \cdot \frac{V \cdot ad}{R \cdot db} \text{ or } K = \frac{M \cdot R \cdot db}{V \cdot ad}$$

If we now measure another liquid of the dilution *v*, its molecular conductivity will be

$$\mu = K \frac{v \cdot ad}{R \cdot db}$$

The cells used for measuring conductivities are of different construction according to their size, for it is found that resistances below 10 or above 10,000 ohms cannot well be measured in the same apparatus. For liquids

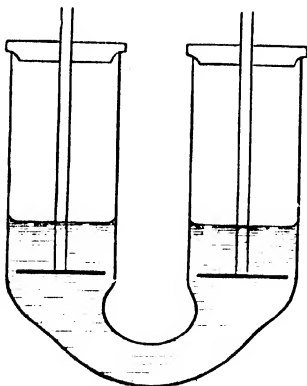


FIG. 55.

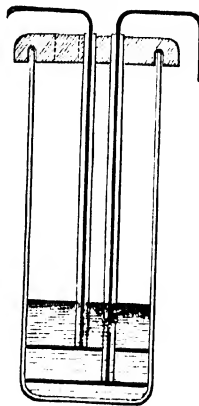


FIG. 56.

that are good conductors we therefore choose cells in which the electrodes are a considerable distance apart, and the column of liquid between them of small section; for bad conductors the conditions must be reversed. The accompanying diagrams (Figs. 55, 56) show two forms that suffice in almost all cases. The electrodes, which must have a section of at least 10 sq. cm., are made of platinum, and should be coated with platinum black by

electrolysing a very dilute solution of platinum chloride between them, with occasional change of direction of the current, until their surface is covered with a black velvety coating.

The following general relations have been found with regard to electric conductivity.

The conductivity of equivalent (not molecular) quantities of the neutral salts is of much the same order of magnitude, varying between 50 and 120, calculating as above and using mercury units. It increases slowly with dilution and usually reaches a maximum at dilutions at about 2000 litres. The following table, containing values observed by Kohlrausch, shows this in detail; the temperature of observation was 18°.

Dilution.	KCl	NaCl	LiCl	$\frac{1}{2}$ BaCl <sub>2</sub>	$\frac{1}{2}$ K <sub>2</sub> SO <sub>4</sub>	$\frac{1}{2}$ MgSO <sub>4</sub>
1 l.	91.9	69.5	59.1	65.8	67.2	27.0
10 l.	104.7	86.5	77.5	86.1	89.7	47.4
100 l.	114.7	96.2	87.5	100.6	109.8	71.5
1,000 l.	119.3	100.8	92.1	109.2	120.7	93.5
10,000 l.	120.9	102.9	94.3	112.6	124.9	103.4
50,000 l.	121.7	102.8	95.5	114.4	126.6	105.2
100,000 l.	121.6	102.4	96.5	114.2	127.5	105.6

This table presents us at the same time with another regularity. The increase of conductivity with increasing dilution is different according to the nature of the salts. The conductivity of salts with two univalent ions changes least, the change is greater for salts with one bivalent and two univalent ions, and greatest of all for magnesium sulphate, which contains two bivalent ions. This rule has been proved to hold very generally.

The principle of greatest generality regulating the conductivity of neutral salts is not, however, to be seen in the preceding small table. It was discovered by Kohlrausch in 1876 and may be expressed most shortly as follows:—The conductivities of the neutral salts are additively composed of two values, one depending only on the metal or positive ion, the other only on the acid radical or negative ion.

The form of this law agrees exactly with the law of thermo-neutrality and the laws for the volume and most of the other properties of salt-solutions. The reason is the same as before; the mutual independence of the conductivity of the two ions, as stated in the law, proves the corresponding mutual independence of the ions themselves.

If we attempt to represent to ourselves what goes on in the interior of an electrolyte when a current is passing, we arrive at something like the following view. The electrical motive-power which, in consequence of the difference of potential always present in the circuit, acts on the positive ions in the direction of the positive current and on the negative

ions in the reverse direction, serves to set these ions in motion so that they transport electricity in corresponding paths. The conductivity (in other words, the quantity of electricity conveyed in unit time in virtue of unit electromotive-force) evidently depends on the number of the moving ions and on the speed at which they move. We must remember too that according to Faraday's Law equivalent ions, no matter what their composition, transport the same quantity of electricity. If therefore we perform our calculations for equivalent quantities of the different electrolytes, as was done in the definition of the equivalent conductivity, these quantities will transport equal quantities of electricity, and the equivalent conductivity is thus a direct measure of the velocity of migration of the ions.

Here, to be sure, we make the assumption that all the molecules contained in solution take part in carrying the electricity—an assumption not always justified. With dilute salt-solutions, however, this is so nearly the case that we may neglect any deviations from it, meanwhile at least.

From the difference in the conductivity of dilute salt-solutions we perceive that the velocities of migration of the ions must be different. The fact that the conductivity of potassium chloride, bromide, etc., exceeds that of sodium chloride, bromide, etc., by 18 to 19 units shows that the potassium ion must migrate 18 to 19 units faster than the sodium ion. In the same way we can ascertain the differences between the velocities of other ions; the velocities themselves, however, cannot be determined from the conductivity.

We come here upon a phenomenon first rightly understood by Hittorf (1853). If during electrolysis the two ions (as had always been tacitly assumed) migrate at the same rate, then the loss experienced by the liquid must be equally large at the two electrodes, and the concentration round these must be equally diminished. This is in general not the case; the concentrations change unequally at the two electrodes, and from this Hittorf concluded that the two ions migrate at different rates.

In order to make the action of the different rates of migration clear let us consider Fig. 57. The black points represent one ion, the white circles the other. During electrolysis the black points move to the left, the white to the right; the former moving twice as fast as the latter. The top row represents the condition before electrolysis, the following rows a series of conditions during electrolysis. The heavy vertical line divides the original system into two equal parts.

At the beginning of the electrolysis there are on each side seven black and seven white ions. At the conclusion, after six molecules have been decomposed, there are five undecomposed molecules on the left hand and only three on the right hand: the concentration has become different on the two sides. The number of black ions on the

left has increased from seven to eleven, *i.e.* by four; the number of white ions on the right from seven to nine, *i.e.* by two. These increments are proportional to the rates of migration.

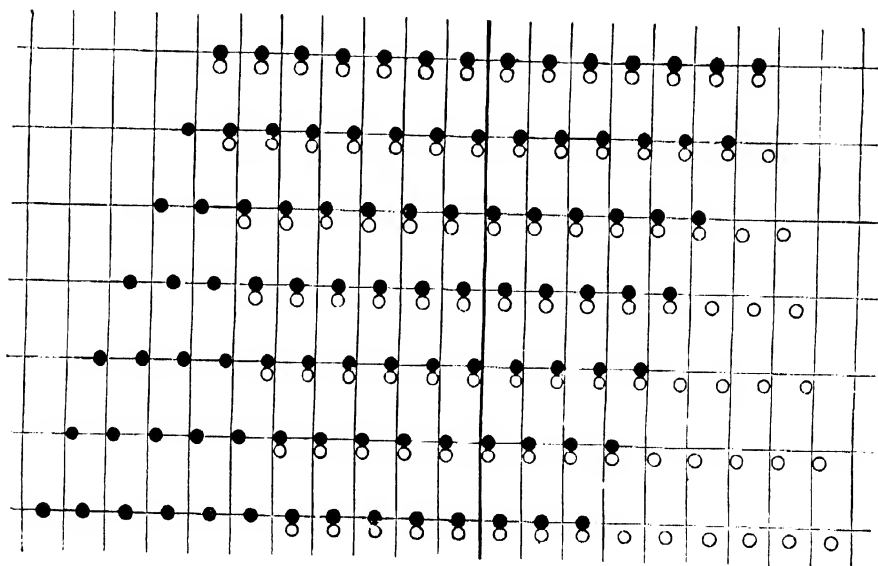


FIG. 57.

Accordingly, if we determine, after electrolysis, the increase of the positive and negative ions at the corresponding electrodes, the ratio is equal to the ratio of the velocities of migration.

It is now easy to ascertain the share of the different ions in the conductivity. On the electrolysis of a solution of potassium chloride, for example, the concentrations at the two electrodes remain almost exactly equal; consequently the ions K and Cl move at the same rate, *viz.* (if we use the units of p. 281) 59.7 in solutions of 1000 l. dilution. From this it follows at once that the rate of migration of sodium is 41.1, of lithium only 32.4, etc.

By determining a single ratio of transport, *e.g.* that of potassium chloride, we can calculate the velocities of all the ions, provided the conductivities are known; and, if we know the latter, we can at once proceed backwards to the ratios of transport of all the salts formed of these ions. Kohlrausch has shown that the results of such a calculation agree most completely with the direct determinations of the ratios of transport made by Hittorf.

The strong acids of the type of hydrochloric and nitric acids behave similarly to the neutral salts, their conductivity, however, being much greater. As the velocity of the negative ions is known, the greater conductivity can only be due to the great velocity of the hydrogen ion. The following table contains the equivalent conductivities at 18° of a few acids measured by Kohlrausch:—

Dilution.	HCl	HNO <sub>3</sub>	$\frac{1}{2}$ H <sub>2</sub> SO <sub>4</sub>	$\frac{1}{3}$ H <sub>3</sub> PO <sub>4</sub>	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>
1 l.	278.0	277.0	188.9	29.0	1.2
10 l.	324.4	322.5	208.4	43.0	4.3
100 l.	341.6	339.5	285.5	79.0	13.2
1000 l.	345.5	342.7	331.6	96.8	38.0

At a dilution of 1000 l., when chlorine has a velocity of 59.7, we get for the hydrogen of hydrochloric acid, and consequently for hydrogen in general a velocity of 285.8. Hydrogen therefore migrates five times as fast as chlorine.

Great changes of concentration must thus appear at the electrodes when acids are electrolysed. These changes have also been measured by Hittorf, and Kohlrausch has shown that they are in perfect concordance with the theory of the independent migration of the ions.

Kohlrausch gives the conductivity of bases at 18° as follows—

Dilution.	KOH	NaOH	NH <sub>4</sub> OH
1 l.	171.8	149.0	0.84
10 l.	198.6	170.0	3.1
100 l.	212.4	187.0	9.2
1000 l.	214.0	188.0	26.0

From the velocity of migration of potassium, which is 59.7, it follows that the velocity of hydroxyl OH is 154.3, which therefore migrates considerably faster than the other negative ions, *e.g.* about 2.5 times as fast as chlorine—one of the next fastest.

While the strong acids and bases thus obey the law of Kohlrausch, the weak acids and bases diverge from it exceedingly. Neither phosphoric acid, nor acetic acid, nor ammonia gives numbers that can be brought into harmony with the law, for their conductivities are smaller than the velocity of migration of hydrogen on the one hand, and hydroxyl on the other, so that even the assumption that one of the ions did not move at all would still give much larger numbers than those observed.

The explanation of these abnormalities may be found in the fact that we have neglected in our last considerations a factor of the conductivity which has been already indicated. The molecular conductivity can only be represented as the sum of the velocities of migration of the ions, when the number of ions conveying electricity is in all cases the same. Now it is true that we have compared solutions containing equivalent quantities of the different electrolytes, but we have still to find out whether equal numbers of free ions are contained in these equivalent quantities, for the ions alone are active in the conduction of electricity.

Determinations of the freezing-point of solutions show that hydrochloric acid and potash exert an influence almost twice as great as that which corresponds to their molecular weight—they are thus almost completely dissociated into their ions. Acetic acid and ammonia, on the other hand, depress the freezing-point almost as indifferent sub-

stances, *i.e.* as calculated from their molecular weight—very few free ions exist in them. Phosphoric acid lies between the two, but nearer acetic acid than hydrochloric acid; it is thus partially, but still very far from fully, dissociated into its ions.

Consequently the law of Kohlrausch is not to be written in the form  $\mu = u + v$ , where  $\mu$  is the molecular conductivity and  $u$  and  $v$  the velocities of migration of the ions, but in the form

$$\mu = x(u + v),$$

$x$  representing the portion of the electrolyte dissociated into its ions. Only on infinite dilution does the dissociation become complete, when the corresponding conductivity  $\mu_{\infty}$ ,  $x$  being 1, is given by the equation

$$\mu_{\infty} = u + v.$$

The law of Kohlrausch therefore only holds strictly for infinitely dilute solutions.

It has been already mentioned (p. 281) that the salts, especially those with univalent ions, are as good as completely dissociated at dilutions practically attainable (at about 1000 l.); further dilution does not alter their condition. The same applies to strong acids and bases. For these substances therefore we can determine  $\mu_{\infty}$  with sufficient approximation. The salts of weak acids with strong bases and of weak bases with strong acids behave similarly to salts with both components strong. Consequently by investigating such salts we can ascertain the velocity of migration of weak acids and bases, so that this property is accessible to measurement for all ions whatsoever.

If we are thus in possession of this knowledge of the values of  $u$  and  $v$  for every electrolyte, we can easily calculate the portion  $x$  of the electrolyte dissociated into ions, or the degree of electrolytic dissociation, from the equations

$$\begin{aligned}\mu &= x(u + v) \\ \mu_{\infty} &= u + v;\end{aligned}$$

for by division we obtain

$$x = \frac{\mu}{\mu_{\infty}}.$$

The degree of dissociation of a dissolved electrolyte at any state of dilution is equal to the ratio of the molecular conductivity at this state to the molecular conductivity at infinite dilution.

The degree of dissociation determined in this way agrees completely with that ascertained from the depression of the freezing-point. The determination from the electric conductivity, however, is incomparably more exact, so that the principle just stated is the most important aid towards obtaining the value of  $x$ . This magnitude is of extraordinary significance, as will be shown in the last portion of this book. It is a measure of the activity of a substance, *i.e.* a measure of its chemical affinity.



In conclusion, a few empirical relations between the velocities of migration of the different ions may be indicated.

Of the univalent metals, potassium, caesium, and rubidium move most rapidly, and all three at about the same rate: sodium moves considerably more slowly, lithium is still slower. Ammonium has the same velocity as potassium, and thallium is not far removed from these; silver comes very near sodium.

Amongst the bivalent metals, calcium, strontium, and barium move with nearly the same speed; magnesium is slower, and is followed closely by zinc, copper, and the other "vitriolic" metals.

Chlorine, bromine, and iodine are among the fastest univalent acid radicals and are almost equal in speed. The radical of perchloric acid,  $\text{ClO}_4$ , moves even more rapidly than these, and with decreasing velocity is followed by  $\text{ClO}_3$ ,  $\text{BrO}_3$ , and  $\text{IO}_3$ . The radical of nitric acid resembles chlorine. Fluorine possesses a considerably smaller velocity, a property which seemingly belongs generally to the members of the natural families of the elements with low atomic weight.

The radicals of the compound organic acids move more slowly the more atoms they contain. In comparatively simple radicals the nature of the elements is of decided influence; thus chlorine diminishes the velocity, while sulphur increases it. But when the number of atoms in the radical exceeds twelve this influence disappears almost entirely. The velocity of migration then seems to depend only on the number of atoms, and increases on the addition of new atoms the more slowly, the more atoms there are already present.

No constitutional influence has been recognised, isomeric ions, *e.g.* those of butyric and isobutyric acid, moving with equal rapidity.

The bivalent and multivalent acid radicals have been but little investigated. Selenic and sulphuric acids have very nearly the same velocity; and so have phosphoric and arsenic acids. The radicals of the polythionic acids seem to have velocities increasing with the quantity of sulphur they contain, but very little is known with certainty in this respect.

The influence of temperature does not vary much. It is mostly 2 per cent per degree; being somewhat larger with small velocities of migration, and conversely.

## CHAPTER V

### CHEMICAL AND ELECTRICAL ENERGY

IN discussing Faraday's Law it was emphasised (p. 270) that the quantity of electricity set in motion in galvanic cells is always the same if equivalent quantities of the reacting substances in the cells have been chemically transformed. But the energy that is set free in such reactions, and which is usually measured by the corresponding development of heat, has very different values. As electrical energy is equal to the product of quantity and electromotive-force, and as the first factor is the same for equivalent processes in the cells, it follows that the electromotive-force of the various galvanic elements should be proportional to the heat developed by the reactions taking place within them.

As we learned on p. 272, 96,540 coul. are set in motion by a chemical action between gram-equivalents; and further the unit of electrical energy, volt  $\times$  coul., is equal to .241 cal. (p. 269). If we call the development of heat corresponding to the chemical process  $H$ , then, if the chemical energy is completely transformed into electrical,  $H = Eq$ ,  $q$  being the quantity of electricity. Heat is here measured in the same units as electrical energy; the customary unit, the calorie, is as we saw above  $\frac{1}{.241}$  greater. The quantity of electricity is 96,540 coul. Therefore, if we measure the heat in calories

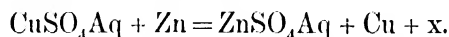
$$\frac{H}{.241} = E \times 96,540$$

$$E = \frac{H}{23,267}$$

If we measure the heat, as we did in the chapters on thermochemistry, in the more convenient K-units, 100 times greater than the small calorie, we have

$$E = \frac{H}{232.67} = .004298 H.$$

In Daniell's element the chemical process is the substitution of zinc for copper in the sulphate. We have



If we introduce the heats of formation with changed sign into this equation (pp. 233-234), we obtain the heat of reaction.

$$-1984 = -2485 + x$$

$$x = 501 \text{ K.}$$

This, however, is for a gram-atom of metal, *i.e.* for two gram equivalents, so that the heat of reaction for one equivalent is 250.5 K. The electromotive-force corresponding is, in volts,  $250.5 \times 0.04298 = 1.074$  V. In reality the electromotive-force of a Daniell cell is found to come very near this value, and so it was concluded that the chemical energy of galvanic elements was in general completely converted into electrical energy.

Further investigation, however, has shown that such is not always the case. There are elements with smaller, and also some with greater electromotive-force than corresponds to the above calculation, so that *a priori* nothing definite can be said as to the relation between the two values.

We are able, however, to state between these two magnitudes (chemical and electrical energy) and the alteration of electromotive-force with the temperature, a relation by means of which one of the three can be calculated if the other two are known. To find this we

adopt precisely the same mode of reasoning as we used in finding the relation between the alteration of vapour-pressure with the temperature, and the latent heat of vaporisation.

Let there be given a galvanic element whose chemical energy (or heat of reaction) for one equivalent is equal to  $H$ . Let the electromotive-force be  $E$ , and let the quantity of electricity developed

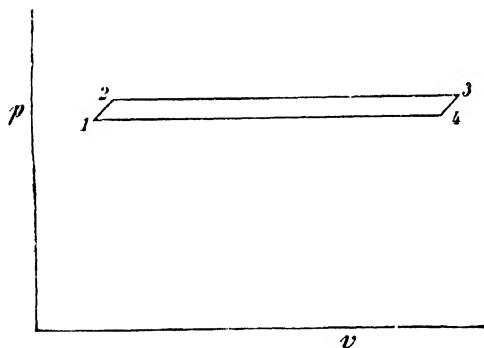


FIG. 58.

by one equivalent of the reacting substances (96,540 coul.) be denoted by  $q$  for the sake of brevity. Suppose the galvanic element to have the electromotive-force  $E$  at the temperature  $T$ ; and let this value be denoted in a system of co-ordinates, in which the abscissæ are quantities of electricity and the ordinates electromotive-forces, by the point 1. We raise the temperature to  $T + dT$ , where  $dT$  signifies a very small change of temperature. The electromotive-force owing to

this will increase, say, by  $dE$ . The element is now allowed to work until the quantity  $q$  has been developed. The state of the element is then given by the point 3. Now let us lower the temperature again to  $T$ , arriving thus at the point 4, and send the quantity  $q$  into the element in the opposite direction. By this the first chemical process (if it is of the type of that taking place in a Daniell cell) will be undone and the element arrive exactly at its initial state.

The work performed in this reversible cycle is  $q \cdot dE$ , and is numerically equal to the area of the quadrilateral 1, 2, 3, 4. The heat conveyed to and from the element in the process must be  $Eq - H$ ; for the energy  $Eq$  is associated with the electrical process, which, however, takes place along with a chemical process giving out the energy  $H$  (the heat of reaction), so that there only remains to introduce the difference  $Eq - H$ .\*

We have again to make use of the relation between the heat transformed into work and the temperature (p. 249), and so obtain

$$\frac{dT}{T} = \frac{q \cdot dE}{Eq - H}$$

or 
$$\frac{dE}{dT} = \frac{Eq - H}{qT}$$

The difference  $Eq - H$  signifies, as we have mentioned, the heat which must be communicated to the element in order that it may be maintained at a constant temperature while it is at work,—or the difference between the electrical and chemical energy. If this is equal to zero as in Daniell's element, then the left-hand side of the equation is also zero, and therefore, as  $dT$  cannot become infinitely large,  $dE$  must vanish altogether. Such an element, in which the chemical energy passes wholly into electrical energy, does not alter its electromotive-force with change of temperature.

If  $Eq - H$  is positive, *i.e.* if the electrical energy is greater than the chemical, then, when the element is active, heat must be communicated to it, or else it cools down. In this case  $dE$  is also positive, and so the electromotive-force is increased by raising the temperature. If, on the other hand,  $Eq - H$  is negative, the chemical energy being greater than the electrical, the element becomes heated while doing work:  $dE$  is then negative, and so the electromotive-force is diminished by heating.

All these conclusions have been confirmed by recent researches, especially by those of H. Jahn (1888). The equation itself was given by Willard Gibbs and von Helmholtz.

\*  $H$  must of course be given in "electrical calories," one of which is equal to .241 cal.

The question as to the circumstances that determine whether  $E_q$  shall be equal to, greater, or less than  $H$  has not yet been fully answered. The electrical and chemical process in a Daniell cell is at least twofold: there is formation of zinc sulphate and decomposition of copper sulphate. Accordingly the electrical work  $E_q$  is composed of two parts, an electromotive-force having its source at each seat of chemical action. We are only now beginning to acquire our first rudimentary knowledge of the magnitude of these electromotive-forces and the corresponding chemical changes, so that the foundations of a theory of galvanic elements taking sufficient account of these separate values are just being laid.

# BOOK X

## CHEMICAL DYNAMICS

### CHAPTER I

#### CHEMICAL KINETICS

WHEN C. F. Wenzel in 1777 set himself to the task of investigating the cause of chemical processes, or the laws of chemical affinity, he had first of all to search for a method of measurement. In analogy to the method adopted for measuring the causes of mechanical processes or of motion, he chose to measure chemical forces by the velocities with which they effected analogous processes.

The conception of "chemical velocity" is defined as the ratio of the amount of substance transformed in the process under consideration to the time required for its transformation. For example, the expression that fermentation proceeds faster at a high temperature than at a low one means that *ceteris paribus* more sugar is converted in a given time into alcohol and carbonic acid at a high temperature than at a low temperature. This chemical velocity has little more than an external similarity to mechanical velocity, and we must therefore be careful not to look upon the similarity as going deeper.

The quantity of substance decomposed in unit time—the rate or velocity of a chemical reaction—is obviously dependent on very many separate circumstances. Wenzel, who wished to measure the affinity of acids for metals, performed his experiments so that the surfaces of the pieces of metal which he exposed to the action of acids were of equal size, for he reasoned that the metal dissolved in a given time must be proportional to its exposed surface. He also saw clearly that the action of his dilute acids would vary with their concentration, the action being in fact proportional to the concentration, "for if an acid liquid dissolve a drachm of copper or of zinc in an hour, a liquid half

as strong will require two hours to effect the same, provided that the surfaces and the heats be equal in the two cases."

The principle thus enounced by Wenzel, that the action is proportional to the active mass, is in reality the fundamental principle of chemical dynamics. Berthollet stated it later and independently of Wenzel, but it is only quite recently that it has experienced the application to the measurement of "chemical forces" foreseen by the latter investigator.

In the first place, it is clear that one of the complications of Wenzel's experiments may be avoided by relinquishing the employment of solid substances. Chemical processes may be instituted in homogeneous liquids and gases, where there is no question of surface at all. It is true that here the course of the processes is not always easy to follow and measure, but still in many cases this is practicable.

The first of such measurements were made in 1850 by Wilhelmy, who correctly stated the law of the progress of a certain class of chemical reactions. If only one substance is affected in the process within a homogeneous fluid, it is manifest that the velocity cannot remain constant, but must continually decrease; for supposing one-tenth of the substance present to be transformed in unit time, we should get a table like the following to show the course of the reaction—

Time.	Substance present.	Substance transformed.
0—1	1·000	·100
1—2	·900	·090
2—3	·810	·081
3—4	·729	·073
4—5	·656	·066

At the commencement the amount 1·000 is present, and after the lapse of unit time ·100 has been transformed according to our assumption. The amount ·900 is now left, of which a tenth, this time ·090, again undergoes transformation. The quantity remaining behind is now  $·900 - ·090 = ·810$ , of which again a tenth or ·081 is transformed, and so on.

The law of this transformation is easily stated—As the time increases in arithmetical progression the substance present decreases in geometrical progression.

Let us give the preceding table a general form by putting the fraction transformed in unit time not equal to ·1, but equal to  $a$ . We obtain

Time.	Substance present.	Substance transformed in unit time.
0—1	1	$a$
1—2	$1 - a$	$(1 - a)a$
2—3	$1 - a - (1 - a)a = (1 - a)^2$	$(1 - a)^2a$
3—4	$(1 - a)^2 - (1 - a)^2a = (1 - a)^3$	$(1 - a)^3a$
4—5	$(1 - a)^3 - (1 - a)^3a = (1 - a)^4$	$(1 - a)^4a$

If we therefore denote by  $\theta$  the interval from the commencement of the process, the amount of substance still present at the time  $\theta$  is  $(1-a)^\theta$  and the quantity transformed in the next time-unit is  $(1-a)^\theta a$ ; and if we put, in general,  $x$  for the quantity transformed,  $1-x$  being the quantity still unchanged, we obtain  $1-x=(1-a)^\theta$ , which is the algebraic expression of the above relation.

The equation, however, has been deduced on an inexact assumption. We have so conceived the process as if the transformation took place in the consecutive units of time at a uniform velocity, and changed suddenly at the beginning of the next unit, corresponding to the diminished amount of substance present. Now this is not what really occurs, for the change evidently proceeds continuously; we can, however, approximate closely to the actual process by choosing the units of time and the fraction  $a$  as small as possible, *i.e.* by making both indefinitely near zero. Then it is true the quantity  $(1-a)^\theta$  cannot be evaluated by elementary mathematics, for it becomes  $(1-0)^\infty$ , a approaching indefinitely near zero, and  $\theta$ , the number of the indefinitely small time-units in a finite time, *e.g.* in an hour, being infinitely great. From higher mathematics we learn that in this case the expression  $(1-a)^\theta$  becomes equal to  $e^{-a\theta}$ ,  $e$  being as before (p. 71) the number 2.71828. We have therefore  $1-x=e^{-a\theta}$ , or, if we take the logarithm to the base  $e$  of both sides,  $\lg(1-x)=-a\theta$ , or  $-\lg(1-x)=a\theta$ , or, lastly,  $\lg \frac{1}{1-x}=a\theta$ . Here, again,  $\lg$  denotes the natural logarithm,  $\theta$  the number of time-units expired from the commencement of the reaction, and  $a$  the fraction of the initial substance transformed in unit time. In chemical dynamics it is customary to take the minute as time-unit. If therefore we count the time  $\theta$  in minutes,  $a$  is the coefficient of velocity of the reaction.

To test the accuracy of the equation  $\lg \frac{1}{1-x}=a\theta$  we do not require to get the natural logarithm  $\lg$  of  $\frac{1}{1-x}$ ; the ordinary decimal logarithms are proportional to the natural logarithms, being always 2.3026 times smaller, so that we can write the equation

$$\log \frac{1}{1-x} = .4343a\theta.$$

Wilhelmy first showed the validity of this formula in the case of the inversion of cane-sugar, which decomposes under the influence of free acid into dextrose and levulose, by taking up the elements of water, thus:  $C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$ . Here the acid suffers no change, and the water in such experiments is always present in so great excess that the alteration of its quantity is quite inappreciable. The conditions for the deduction of the equation are therefore fulfilled. In order to determine the quantity of unchanged cane-sugar present at any time, he took advantage of the rotation of the plane of polarisation by the sugars, which thus enabled him to perform the analysis without



any chemical disturbance of the state of the system. He obtained, for example, the following series of numbers—

$\theta$ (Minutes).	Angle.	$\log \frac{1-x}{1}$	$\frac{1}{\theta} \log \frac{1}{1-x}$
0	46·75°	—	—
15	43·75°	·0204	·00136
30	41·00°	·0399	·00133
45	38·25°	·0605	·00134
60	35·75°	·0799	·00133
75	33·25°	·1003	·00134
90	30·75°	·1217	·00135
105	28·25°	·1441	·00137
120	26·00°	·1655	·00137
$\infty$	—18·70°	—	—

The observations are calculated as follows:—The original sugar-solution had the rotation 46·75°; after it had been completely converted into dextrose and levulose its rotation was —18·70°. As the rotation is proportional to the quantity of sugar present, the total angle traversed, viz. 46·75° + 18·70° = 65·45°, is the measure of the total amount of sugar. The angle after the expiry of 15' is 43·75° showing a decrease of 3·00°; the fraction  $x$  which has been transformed is therefore  $\frac{3\cdot00}{65\cdot45}$ , while  $1-x$  is equal to  $\frac{62\cdot45}{65\cdot45}$ . If we now calculate

$\log \frac{1}{1-x}$  we find it equal to ·0204, and this divided by  $\theta=15$ , the number of minutes from the commencement, gives ·00136.

$\frac{1}{\theta} \log \frac{1}{1-x}$ , given in the last column, is, according to the equation, equal to ·4343  $a$ , and must therefore be constant. As we see from the table, this is actually the case; for the slight variations are merely due to the errors of experiment.

Results similar to those obtained by Wilhelmy for the inversion of cane-sugar have appeared later in the investigation of a great number of other chemical processes. For example, the reduction of permanganic acid by a great excess of oxalic acid, the hydrolysis of a dilute solution of methyl acetate into methyl alcohol and acetic acid in presence of acids, the conversion of dibromosuccinic acid into hydrobromic acid and bromomaleic acid, of monochloracetic acid into glycollic acid, the transformation of atropin into hyoseyamin by alkalis—all these proceed according to the same law, which in no way depends on the substances taking part in the reaction: whenever a chemical process takes place, so that the amount of one substance only is changed, then it proceeds according to the formula  $\lg \frac{1}{1-x} = a\theta$ . This again is merely a mathematical deduction from the principle

that the chemical action is proportional to the active mass. Of course, by active mass, or concentration, we do not mean the whole amount of substance, but the amount in unit volume; and it should at once be understood that quantities in chemical dynamics are not measured by their absolute, but by their molecular weights. The amount 1 will thus represent 34.46 g. of hydrogen chloride, or 40.0 g. sodium hydrate, etc. The concentration or active mass 1 would therefore be a solution containing a molecular weight in grams in unit volume (c. cm.) As such solutions, however, cannot in general be prepared, the unit of active mass is usually taken a thousand times smaller, a molecular weight being contained in a litre of solution.

Every chemical process such as the above is determined, as we see from the foregoing, by a single constant  $a$ , which is the measure of its velocity; when this is given we know the whole course of the reaction. Theoretically speaking, the reaction never comes to an end; experimentally, however, the termination is easy to observe. A simple calculation, which may be left to the reader, shows that after a period ten times as long as the time required for half the substance to be transformed, only .001 of the original quantity remains unchanged; now this is an amount in general not determinable by the methods of analysis ordinarily employed, and may therefore be neglected without more ado.

We come to a second kind of chemical process, regulated by a new law, when in its course two substances undergo change of quantity. We must again assume that the action is proportional to the amount of each present. From this it follows that the action is proportional to the product of the two quantities; for this is the only function that fulfils the condition.

Let us consider first the simplest case in which the two reacting substances are present in equivalent quantities, which are then numerically equal, each being  $A$  for example. The elementary calculation of the connection between the interval expired and the amount of the undecomposed substances still present at the end of that interval is so tedious and so little convincing that it may be spared the reader. By means of higher mathematics, on the other hand, we can at once deduce the following relation from the condition given—

$$\frac{1}{A-x} - \frac{1}{A} = a\theta.$$

Here  $A$  is the active quantity of each of the two substances,  $x$  the quantity transformed at the time  $\theta$ , and  $a$  a constant which is the measure of the velocity. By an easy transformation we can write the equation in the form

$$\frac{x}{A-x} = Aa\theta$$

which is shorter, but not so convenient as the first for purposes of calculation.

An example of such a process is to be found in the saponification of ethyl acetate by caustic soda, investigated by R. Warder (1881).

$\theta$	$A - x$	$\frac{x}{A - x}$	$Aa$
0	16.00	—	—
5	10.24	.563	.113
15	6.13	1.601	.107
25	4.32	2.705	.108
35	3.11	3.69	.106
55	2.31	6.94	.108
120	1.10	13.55	.113

In the last column we have the values of  $\frac{1}{\theta} \left( \frac{x}{A - x} \right) = Aa$ , which according to theory ought to be constant. In this case also the slight deviations only arise from experimental errors. What was said with regard to processes of the first kind applies equally to processes of the second. The constant  $a$  is determined only by the nature of the substances present, the temperature, and the concentration; if we know its value, the whole course of the reaction is fully specified.

When the two reacting substances are not present in the same concentration or active quantity, the equation is somewhat more complicated, and still more unsatisfactory to deduce in an elementary manner. The result is, if the two concentrations are denoted by  $A$  and  $B$

$$\lg \frac{B(A - x)}{A(B - x)} = (A - B)a\theta.$$

This equation also has been tested and found to agree with experiment.

It appears still conceivable that more than two substances might be requisite for a chemical process. The appropriate equations may be easily developed by higher mathematics, but as no actual case of this has been studied, we need not discuss them here.

The types of chemical processes described in the preceding pages by no means comprehend all that actually occur. They are rather limiting cases, approached more or less closely by the phenomena, but, strictly speaking, never reached.

In the first place, the simplicity and uniformity of the reaction assumed in the calculation are really very seldom to be met with. Several processes almost always take place simultaneously, and only when one has a great numerical preponderance is an apparently simple process observed. This is what meets us everywhere in nature, several actions taking place at the same time in nearly every observed case, it being only possible to fix the laws for a single action by eliminating

the others as completely as possible either by the arrangement of our experiments or by calculation.

In chemistry, as elsewhere in the exact sciences, we overcome this difficulty through the principle of the mutual independence of different processes. We know that if any forces act upon a material particle, each force produces a relative motion independent of all the other forces. In the same way, chemical processes take place, if several come into play between the same substances, according to the laws which were developed above for simple processes. The only difference is that the equations representing the resultant course of all the reactions receive a more complicated form; they can all, however, be deduced from the law of the action of mass (p. 292).

A second circumstance that often determines deviations from the simple formulæ is to be found in the variation of the constant  $a$ . As long as the conditions of the process remain the same,  $a$  can only have one definite value; but new substances are often formed in the course of the process itself, and these may so influence the substances already present, between which the primary reaction takes place, that the velocity of the reaction will change. If such is the case, we can sometimes formulate these disturbing actions also as functions of the quantities of the newly-formed substances, and take them into account in our calculations according to the above-mentioned principle of coexistence. But this is not always successful, and then we are compelled to have recourse to mathematical artifices, which give an approximate solution of the problem. The same thing often occurs in astronomy, for instance. The mode of procedure in the separate cases, however, would take us far beyond the limits of such a work as this, so that the student must be content with a simple indication of the fact.

## CHAPTER II

### CHEMICAL EQUILIBRIUM

MANY chemical processes are reciprocating, *i.e.* the original substances may be reobtained from the products of the reaction. The result of such opposed processes is a state of chemical equilibrium—a state in which both the original and the newly-formed substances are present in definite quantities, which so long as the conditions remain the same do not undergo further change.

The condition for chemical equilibrium may be stated in this way, that the rate at which each substance is formed must be equal to the rate at which it is decomposed; its quantity then remains unchanged.

The simplest case is when a single substance experiences such changes. Let  $p$  be the original quantity of the first substance,  $p'$  of the second. According to the fundamental principle of the action of mass, the rate at which the first substance is converted into the second is at each instant proportional to the quantity of it present. If the amount already transformed is  $x$ , then  $p - x$  is the amount still present and  $u = c(p - x)$  where  $c$  is the constant of velocity of the process. The quantity of the second substance is at the same time  $p' + x$ , for so much is gained by it as was lost by the first. The rate at which it changes into the original substance is therefore  $u' = c'(p' + x)$ , and equilibrium is established when both rates are the same. From  $u = u'$  it follows that

$$c(p - \xi) = c'(p' + \xi)$$
$$\frac{c}{c'} = \frac{p' + \xi}{p - \xi}.$$

Here and in the sequel the value of  $x$  for which the system is in equilibrium is denoted by  $\xi$ . We may express the result thus—in the case where one substance is transformed into one other, the reaction being reciprocating, equilibrium is established when the quantities of the two substances are in a definite ratio, which is equal to the inverse ratio of the constants of velocity of the opposed reactions. This ratio is perfectly independent of the amounts  $p$  and  $p'$  originally present.

If we thus know the coefficients of velocity of the opposed reactions, we can calculate from them the proportions for equilibrium. On the other hand, from the measurement of the equilibrium-ratio we only obtain the ratio of the velocities, not their absolute value.

Examples of this case are rare, and not one has been exactly investigated.

The conditions of equilibrium are considerably simplified when the substances in equilibrium form a heterogeneous system composed of two immiscible portions. Guldberg and Waage (1867) have stated the following principles for this case—the active mass of a solid substance is independent of its quantity. This empirical principle has been found to agree with all the facts, and affords us an easy mode of treating the equations of equilibrium, for we have only to put the value of the active mass of solids in them equal to a constant. The equation  $\frac{c}{c'} = \frac{p' + \xi}{p - \xi}$  becomes  $\frac{c}{c'} = \frac{\pi'}{p - \xi}$  if we assume that the second substance is solid and denote its constant active mass by  $\pi'$ . This equation leads us to the conclusion that equilibrium can only exist when the liquid (or gas) in contact with the solid substance possesses a perfectly definite active mass or concentration.

On comparing this principle with the results of experience we find it confirmed. If a salt dissolves in water, a state of equilibrium is attained when (at a given temperature) the solution is of a definite concentration, which we know is not affected in the slightest degree by the amount of salt present in excess. Another well-known case is that of vaporisation: vapour and liquid are in equilibrium only when the former has a definite pressure or concentration. We usually look upon the pressure as that which is determined by the nature and temperature of the liquid, but as pressure and density are proportional the expression given above is quite as warrantable as the customary one.

Another case of heterogeneous equilibrium is when a gas under a definite pressure is dissolved by a liquid. The gas here plays the part of the solid substance whose active mass is constant, and equilibrium is reached when the concentration of the solution has attained a definite value.

The transformations of allotropic and polymeric modifications possess a more chemical character. Thus, on being heated, paracyanogen  $(CN)_n$  (obtained in the preparation of cyanogen as a brown powder) passes into cyanogen until at a constant temperature a definite value of the pressure or density of the latter is established. Exactly the same laws hold good here as for the mere vaporisation of a solid or liquid substance. If the pressure is increased beyond that of equilibrium the proper amount of cyanogen is converted into paracyanogen to re-establish the original density of the former.

Laws perfectly similar regulate the somewhat more complicated cases of the transformations of cyanic acid  $HO\dot{C}N$ , cyanuric acid  $(HO\dot{C}N)_3$ , and

cyamelide  $(\text{HOCN})_n$ . If cyanic acid vapour is produced by rapid heating of cyanuric acid, for every temperature above  $150^\circ$  there is a definite density (or pressure) of the vapour, for which it is in equilibrium with solid cyanuric acid, just as if we were dealing with vaporisation and not with chemical decomposition. Below  $150^\circ$  the vapour of cyanic acid is not converted into cyanuric acid but into cyamelide, and obeys with regard to the latter exactly similar laws. At  $150^\circ$  cyanuric acid and cyamelide can exist together, and the vapour-pressure of cyanic acid over both is the same.

Similar relations have appeared in the vaporisation of yellow and red phosphorus. The former has a much lower vapour-pressure than the latter, and the matter is somewhat complicated on account of the yellow modification up to its boiling-point and a little beyond this being an unstable form. When it is heated it begins at once to pass into the red modification, so that it is somewhat difficult to get the phenomena belonging properly to the unmixed substances.

A third case of equilibrium of the first order appears when both substances have a constant active mass, *i.e.* are neither gaseous nor in solution. Then in general they can never be in equilibrium, for the ratio of their active masses need not be that of their rates of transformation, so that perfectly definite conditions must obtain for a state of equilibrium to exist at all. Water and ice, for example, are such substances; in general they cannot exist together—only at a definite temperature,  $0^\circ$ , is this possible.\* The same holds good for rhombic and monosymmetric sulphur, for red and yellow mercuric iodide, and for all substances that can exist in two forms, transformable one into the other, according to the temperature.

The equation for this case assumes the form

$$\frac{c}{c'} = \frac{\pi'}{\pi}$$

and can only be satisfied by definite values, as has already been mentioned.

The relations of equilibrium conditioned by processes of the second order (p. 295) are not so simple. If  $u$  is the velocity of any process between the substances  $p$  and  $q$ , then according to the foregoing

$$u = c(p - x)(q - x),$$

$x$  again representing the quantity transformed at any time. Suppose  $p$  and  $q$  to produce two new substances by their interaction, the quantities of which originally present were  $p'$  and  $q'$ ; then at the time for which the above equation holds we have also

$$u' = c'(p' + x)(q' + x),$$

\* This temperature may be slightly altered by changing the pressure (p. 251), but the variations are so small that they need scarcely be considered. In any case this last kind of equilibrium may be looked upon as the limiting case of the preceding kind, and not as being opposed to it.

and equilibrium is reached when  $u = u'$ , or

$$c(p - \xi)(q - \xi) = c'(p' + \xi)(q' + \xi)$$

This equation was first given by Guldberg and Waage (1867) for the mutual action of two pairs of substances. To put it into a more convenient shape, let us make the original quantities of the two substances each equal to 1, and let none of the products of the reaction be at first present. Substituting then in the equation  $p = q = 1$ , and  $p' = q' = 0$ , we obtain

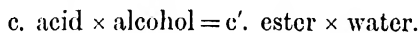
$$c(1 - \xi)^2 = c'\xi^2$$

$$\frac{c}{c'} = \left(\frac{\xi}{1 - \xi}\right)^2$$

Now  $\xi$  is the quantity of the newly-formed, and  $1 - \xi$  the quantity of the original, pair of substances present on equilibrium. The velocities of reaction are therefore inversely proportional to the squares of the quantities for which equilibrium is established if the original substances were in equivalent proportions.

The accuracy of the general formula was first tested by Julius Thomsen (1869), who altered the quantities  $p, q, p', q'$  in many ways, determined  $\xi$  experimentally, and then tried if the observed values could be represented by always using the same ratio  $c : c'$ . The result was satisfactory. A description of the thermochemical method employed will be given later. The substances were hydrochloric acid and sodium sulphate on the one hand, sulphuric acid and sodium chloride on the other, in dilute solution. A series of experiments with nitric acid instead of hydrochloric acid was also performed.

The formula received further confirmation from a previously published research by Berthelot and Péan de St. Gilles (1862), who, however, did not turn it to account in this direction. It was upon the formation of esters (compound ethers) from acids and alcohols, the following equilibrium being established,



Ostwald too (1876) performed a set of experiments with the same substances as Thomsen had employed, but according to another method, that, namely, of change of volume, and obtained results in agreement with the formula.

The general equation

$$c(p - \xi)(q - \xi) = c'(p' + \xi)(q' + \xi)$$

can be gradually simplified by some of the substances present being in such a state that their active mass is constant: 1, 2, 3, or 4 substances in succession may be in this state, so that we have four cases of limited equilibrium of the second order, which will now be considered in detail.

If, for example, the last substance assumes such a state, we have



$q' + \xi = \rho'$ , a constant. At the same time let us put as before  $p = q = 1$  and  $p' = 0$ ; then

$$c(1 - \xi)^2 = c'\xi\rho',$$

or

$$\frac{c}{c'\rho'} = \frac{\xi}{(1 - \xi)^2}.$$

The ratio of the quantity of the newly-formed substance (which is not in a state of constant concentration) to the square of the quantity of the original substances must thus be constant.

No good example for this case is as yet known. It is approximately realised when calcium chloride and oxalic acid act on each other in solution, calcium oxalate and hydrochloric acid being formed. The oxalate separates out as a solid and so has a constant active mass. Careful experiments have shown, however, that with varying quantities of the components the formula is not always satisfied. The reason of this probably is that the coefficients of velocity  $c$  and  $c'$  are not independent of the relative amounts present.

If two substances assume the state of constant concentration, the formula can receive two forms. First,  $q - x$  and  $q' + x$  can become constant, passing into  $\rho$  and  $\rho'$ , so that

$$c(1 - \xi)\rho = c'\xi\rho',$$

or

$$\frac{c\rho}{c'\rho'} = \frac{\xi}{1 - \xi}.$$

This formula reminds one of that obtained for equilibrium of the first order. It states that a constant ratio of the two substances with variable concentration, gaseous or in solution, is required for equilibrium. The quantities of the substances with constant active mass have no effect at all.

The many tests applied to the formula have all proved it to be in accordance with experiment. Thus the experiments of Deville (1871) on the interaction between water-vapour and iron, hydrogen and ferrosoferrie oxide, conform to it. Water-vapour is partially reduced by iron to hydrogen, and at the same temperature hydrogen is oxidised by the ferrosoferrie oxide thus formed. The two processes mutually limit each other, so that at every temperature there exists a definite ratio between water-vapour and hydrogen, for which the mixture suffers no alteration either from iron or ferrosoferrie oxide. The ratio changes with change of temperature, the proportion of hydrogen becoming smaller the higher the temperature rises.

A second example was thoroughly investigated by Guldberg and Waage (1867), viz. the action between barium sulphate and potassium carbonate on the one hand, and between barium carbonate and potassium sulphate on the other. As theory predicts, there is equilibrium when the two variable substances (potassium carbonate and sulphate) are in a constant ratio (4 : 1).

But there is still a second possibility of the active masses of two substances becoming constant: namely, when  $p'$  and  $q'$  are both of constant concentration. Then the equation has the form

$$c(p - \xi)(q - \xi) = c'\pi'\rho',$$

or 
$$(p - \xi)(q - \xi) = \frac{c'\pi'\rho'}{c}.$$

In this case there is equilibrium when the product of the two variable concentrations has a constant value. Examples will be given in the next chapter (on dissociation).

If three of the reacting substances have constant concentration, the equation becomes

$$c(p - \xi)\rho = c'\pi'\rho',$$

$$\frac{c\rho}{c'\pi'\rho'} = p - \xi.$$

On the left-hand side of the equation there are only constant quantities, consequently there can be equilibrium only at one definite concentration of the variable substance. This case is quite similar to that described on p. 299, only here the number of solids has risen to three.

Isambert (1886) investigated a reaction coming under this head. When ammonium chloride is mixed in the solid state with lead monoxide, ammonia is evolved with formation of lead chloride (or perhaps oxychloride) until a definite concentration (pressure) is reached. If the pressure is increased, ammonium chloride is reproduced until the concentration sinks to its former value.

The last case, in which four substances of constant active mass react together, leads in general just as little to a state of equilibrium as when two such substances alone are present—either the one or the other system existing exclusively. Only at some definite temperature can there be coexistence of the two systems, and then they may be in any proportions.

Such considerations as these can evidently be further extended, but we need not occupy ourselves with them here, as the experimental investigation of the more complicated cases is almost entirely wanting. We may only remark in general that the kind of equilibrium in a system of substances capable of reciprocal transformation, depends on the number that are in a state of variable concentration, *i.e.* that are gaseous or in solution. The following table will serve to illustrate this:—

Number of Substances with variable concentration.	Equations of Equilibrium.
0	No equilibrium in general.
1	$p = \text{const.}$
2	$\begin{cases} p = \text{const.} \\ q = \text{const.} \end{cases}$

Number of Substances with variable concentration.	Equations of Equilibrium.
3	$\begin{cases} pp' = \text{const.} \\ q \\ pp'p'' = \text{const.} \end{cases}$
4	$\begin{cases} pp' = \text{const.} \\ qq' \\ pp'p'' = \text{const.} \\ q \\ pp'p''p''' = \text{const.} \end{cases}$
etc.	

The general equation of equilibrium will thus have the form

$$\frac{pp'p'' \dots}{qq'q'' \dots} = \text{const.},$$

where  $p, p', p'' \dots$  are the concentrations of the substances on the one side,  $q, q', q'' \dots$  those on the other side of the chemical equation for the reaction.

## CHAPTER III

### DISSOCIATION

THE term dissociation was introduced by Deville to denote certain phenomena, scattered examples of which had long been known, but which were thoroughly investigated by him for the first time—the decomposition namely of chemical compounds by heat, with formation of gaseous products. In such processes states of equilibrium are attained subject to the general laws discussed in the preceding chapter. They might, therefore, be considered merely as special cases of what we already know, but still the phenomena of dissociation have so much that is peculiar to them that a somewhat comprehensive account may not be undesirable.

The simplest case is when a solid on decomposition evolves a single gas; and it was here that the first regularity was discovered. If, for example, we heat calcium carbonate, then, above  $450^{\circ}$ , carbon dioxide is evolved, the substance behaving exactly as a vaporising liquid. For every temperature there is a definite density or pressure of carbon dioxide, at which the gas is in equilibrium with both calcium carbonate and calcium oxide present as solids.

The same is observed with salts containing water of crystallisation. Several investigators, it is true, have denied the existence of a definite pressure at a definite temperature, but all the recent and more exact researches show the perfect accuracy of that law of dissociation, and in particular, that the pressure is independent of the quantities of the two solids—original and decomposed.

The theory of chemical equilibrium leads to the same result. We are dealing with a reaction between three substances, two with constant and one with variable concentration. The equation of equilibrium, if we put  $u$  instead of  $p - \xi$  for the concentration of the variable substance, retaining  $\pi$  for the substances of constant concentration, becomes

$$c\pi = c_1 u \pi_1,$$

or

$$u = \frac{c\pi}{c_1 \pi_1}$$

On the right-hand side we have only constant values, so that the variable concentration on the left must for any one temperature be constant.

The validity of the equation, however, is dependent on the conditions for which it was developed being maintained. Thus the nature of the substances in the whole range investigated must remain the same. Sodium phosphate,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ , for example, has a definite dissociation-pressure of water-vapour, which at a given temperature does not change although we remove more and more water. But this only holds up to a certain point; when so much water is removed that seven atoms only are left, the pressure suddenly becomes smaller, and remains constant for further removal of water. Under these circumstances, the other hydrated salt,  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ , has been formed, and this has another and smaller velocity of decomposition  $c$ , so that the constant expression on the right-hand side of the equation assumes another value.

Similarly, the equation no longer holds when, during the process, one of the substances suffers further change, thus becoming incapable of taking part in the reverse action. Manganese carbonate, for example, decomposes on heating like calcium carbonate. The manganese oxide formed, however, is partially oxidised at the expense of the carbon dioxide ( $3\text{MnO} + \text{CO}_2 = \text{Mn}_3\text{O}_4 + \text{CO}$ ), and cannot afterwards pass back into the carbonate. In this case, in the equation  $c\pi = c_1u\pi_1$ , the velocity of the reverse action  $c_1$  is 0, so that the constant  $u = \frac{c\pi}{c_1\pi_1}$  is rendered infinitely great, *i.e.* the direct action proceeds without limit.

We can make use of the law of constant dissociation-pressure to obtain information regarding the existence or non-existence of definite compounds. One example—the case of the two hydrated sodium phosphates—has already been given. Other such cases have been studied, in particular the ammonia compounds of the metallic chlorides. If silver chloride be saturated with ammonia, the compound  $\text{AgCl} \cdot 3\text{NH}_3$  is formed, which, at  $48.5^\circ$ , has a pressure of 241.4 cm. of mercury. On continuous removal of ammonia the pressure at first remains unchanged, suddenly, however, to sink to 28.8 cm. This sudden change takes place when exactly half the ammonia has been removed, and the compound  $2\text{AgCl} \cdot 3\text{NH}_3$  remains. On further removal of ammonia the new pressure does not alter until the last portions of ammonia have left the silver chloride.

A second case of dissociation is that of a solid giving off two gaseous substances on heating. Whether the solid is completely transformed into the gases, or whether a residue remains, is of no consequence. We shall take the last case as being the more general. The equation of equilibrium is then

$$c\pi = c_1u_1u_2,$$

where  $\pi$  as before refers to the solid,  $u_1$ , and  $u_2$  to the gases. Separating the variables from the constants we have

$$u_1 u_2 = \frac{c}{c_1} \pi.$$

For equilibrium, then, the product of the two variable concentrations must be constant.

Ammonium hydrosulphide  $\text{NH}_4\text{HS}$ , affords us an example of this case. It is formed of equal volumes of ammonia and hydrogen sulphide, and on heating is reconverted into these. As long as the dissociation of this substance takes place in an exhausted vessel (or one filled with an inactive gas) the phenomena are not to be distinguished from those already described. For on dissociation the two gases are produced in equal volumes, and thus  $u_1 = u_2$ , so that for every temperature there is a definite dissociation-pressure, each gas contributing half.

The matter assumes a totally different aspect, however, if one of the products of dissociation is present as such in the vessel from the beginning. Then there is a much smaller quantity of the hydrosulphide dissociated—the product of the partial pressures of the two components having the same value as before. Thus the pressure of ammonium hydrosulphide was found by Isambert to be 50.1 cm. at 25.1° in an exhausted space. In an atmosphere of 8.6 cm. pressure of hydrogen sulphide, the pressure rose to 50.4 cm. on the introduction of hydrosulphide. Half the increase of 41.8 cm., viz. 20.9 cm., is due to the ammonia, the other half, plus the original pressure, 29.5 cm. in all, is contributed by the hydrogen sulphide. In ammonia of 32 cm. pressure the partial pressures were found to be 13.8 cm. and 45.8 cm. If we write down the product of the partial pressures for each case (the temperature being constant) we obtain—

Hydrogen sulphide.	Ammonia.	Product.
25.05	25.05	627
29.5	20.9	616
13.8	45.8	632

The products agree within the limits of experimental error.

If one of the two gaseous products of decomposition is present in excess, there is, as we must again take occasion to emphasise, no constant dissociation-pressure. On diminution of volume, equal volumes of the two gases disappear by combining to form the solid, and in the remaining gaseous mixture the components are in different proportions from what they were before. Now, as the law is that the product of the partial pressures must be constant, it follows that their sum will increase as the difference between the pressures is greater, *i.e.* as the volume of the uncombined gases grows smaller by their union in equal volumes. Conversely, if the volume be increased, the common pressure will diminish, converging asymptotically to

the value corresponding to the substance in vacuô. In such experiments no attention whatever has been paid to these considerations, and the apparent discrepancies between the measurements and theory are probably in great part due to this.

We have a third case of equilibrium when the solid dissociates into equal volumes of three gases. The corresponding equation is

$$c\pi = c_1u_1u_2u_3,$$

or

$$u_1u_2u_3 = \frac{c\pi}{c_1},$$

*i.e.* a state of equilibrium is reached when the product of the three partial pressures attains a certain definite value.

For the case in which none of the gases formed were present in the vessel from the beginning  $u_1 = u_2 = u_3$ ; and the equation becomes

$$u^3 = \frac{c\pi}{c_1} \text{ or } u = \sqrt[3]{\frac{c\pi}{c_1}},$$

showing no formal difference from the first case of dissociation-equilibrium. Only when the gases are present in unequal volumes is the special nature of this dissociation made evident.

The same formula applies to the case of the solid evolving only two gases, one of these, however, possessing twice the volume of the other. For reproduction of the solid the active mass of the former gas must be twice that of the latter,—the union is one of three molecules, and it makes no difference with respect to the fundamental formula whether these molecules are of the same kind or not. The equation is merely simplified by  $u_2$  becoming equal to  $u_3$ , so that we get

$$u_1u_2^2 = \frac{c\pi}{c_1}.$$

Equilibrium, therefore, is produced by the product of the density of the one gas into the square of the density of the other (*viz.* the gas occupying two-thirds of the whole volume) having a definite value. From this it follows that the presence of the same excess of one or other gas will affect the dissociation-pressure differently, the excess of gas having the larger volume acting much more effectively than the excess of the other.

These interesting relations are illustrated by the behaviour of ammonium carbamate, formed by the combination of one volume of carbon dioxide with two of ammonia [ $\text{CO}_2 + 2\text{NH}_3 = \text{CO}(\text{NH}_2)(\text{ONH}_4)$ ]. Horstmann (1871) and Isambert (1883) have investigated this substance, and find a satisfactory agreement with the theory.

In all the cases of dissociation we have hitherto discussed it has been assumed that a solid substance is dissociated into gases. The original substance may also, however, be a gas. Thus hydrogen iodide on heating decomposes into hydrogen and iodine according to

the equation  $2\text{HI} = \text{H}_2 + \text{I}_2$ . For this case we have, in accordance with the remarks made above,

$$cu^2 = c_1 u_1 u_2,$$

$u$  referring to the hydrogen iodide,  $u_1$  and  $u_2$  to the iodine-vapour and hydrogen. If neither of the latter is present in excess,  $u_1 = u_2$ , and so

$$cu^2 = c_1 u_1^2, \text{ or } \frac{u}{u_1} = \sqrt{\frac{c_1}{c}}.$$

This signifies that at a given temperature the ratio between decomposed and undecomposed hydrogen iodide is independent of the pressure; for we can increase or diminish  $u$  and  $u_1$  in the same proportion without the equilibrium being thereby disturbed. This conclusion has been found by Lemoine to be in close agreement with observation.

If one of the gases is in excess, we have  $\frac{u_2}{u_1 u_2} = \frac{c_1}{c}$ . Here the state of dissociation remains unchanged if the pressure of the hydrogen iodide and the other gases be simultaneously so altered that the former is proportional to the geometric mean of the latter.

We have a second case of completely gaseous dissociation when out of one volume of the original substance there are formed two volumes of the new bodies. As examples of this we may mention phosphorus pentachloride,  $\text{PCl}_5$ , which dissociates into  $\text{PCl}_3$  and  $\text{Cl}_2$ ; the so-called bromide of amylene ( $\text{C}_5\text{H}_{11}\text{Br} = \text{C}_5\text{H}_{10} + \text{HBr}$ ); nitrogen peroxide ( $\text{N}_2\text{O}_4 = 2\text{NO}_2$ ); and iodine ( $\text{I}_2 = 2\text{I}$ ). In the two first examples the gases produced on dissociation are different, in the two last they are identical. As has been shown above, this conditions only a slight alteration in the formula. We have, namely,

$$cu = c_1 u_1 u_2,$$

or if  $u_1 = u_2$  (either from none of the different gases being present from the commencement, or from two volumes of the same gas being evolved) then

$$cu = c_1 u_1^2$$

and

$$\frac{u_1^2}{u} = \frac{c}{c_1}.$$

The equilibrium is here no longer independent of the pressure, for if  $u$  and  $u_1$  are increased in the same ratio,  $u_1^2 : u$  changes its value. This holds for all the following cases. If the pressure experiences no alteration by dissociation, as happens with  $\text{HI}$ , then, conversely, the dissociation is not influenced by it; if, on the other hand, the pressure increases with increasing dissociation, as in the present case, then the dissociation decreases with increase of pressure.

The influence of pressure has been investigated for several of the above examples, and the results have been found to agree with the deductions from the equation. This same equation too has become of great importance in



another direction. It has already been stated (p. 274) that many electrolytes in aqueous solution are decomposed into their ions—are dissociated. Since now substances in dilute solution are governed by the laws for gases, it follows that the laws of dissociation are applicable in this case also. The electrolytes for the most part are substances that undergo dissociation in the way we have just discussed, one molecule of  $\text{HCl}$ , for example, falling into two sub-molecules or ions,  $\text{H}^+$  and  $\text{Cl}^-$ . In reality this law of dissociation has been proved valid with electrolytes to an extent far beyond that attainable in the case of gases. Details will be given hereafter.

It is easy to find the law of dissociation for more complicated cases, but it is needless to dwell longer on the subject, as the experimental investigation is still wanting.

The dissociation of such compounds as nitrogen peroxide, which only change their molecular state, is measured by ascertaining the density. If the density of the original substance be  $d$  and that of the product of dissociation  $d'$ , then generally  $d = nd'$ , if  $n$  is the number of molecules into which one of the original molecules decomposes,—for nitrogen peroxide, therefore,  $d = 2d'$ . Let us denote the observed density of the partially dissociated mixture by  $D$ ; the problem is to calculate from this magnitude the dissociated portion  $x$  of the original gas.

The gaseous mixture consists of  $1 - x$  volumes of the density  $d$  and  $2x$  volumes of the density  $d'$ , the total volume being thus  $1 + x$ . As the density of the undecomposed gas is to that of the mixture inversely as the corresponding volumes, we have  $\frac{d}{D} = \frac{1 + x}{1}$  or  $x = \frac{d - D}{D}$ . In the equation for equilibrium we have to substitute  $(1 - x)p$  for  $u$ , and  $xp$  for  $u_1$ ,  $p$  representing the pressure of the gas supposed undissociated.

## CHAPTER IV

### APPLICATION OF THERMODYNAMICS TO CHEMICAL EQUILIBRIUM

FROM what has been stated in the preceding chapter we are enabled to deduce the laws of chemical equilibrium by using as basis the empirical principle, that the action is proportional to the active mass. And to this we have in addition the special law that the active mass of solids is constant.

These principles, however, are only available on condition that the temperature remains constant: they tell us nothing of the influence of temperature on the state of equilibrium, and how the latter alters with change of temperature.

We must here have recourse to other considerations drawn from quite different departments of science, viz. from thermodynamics, and from the kinetic molecular theory. By suitable application these lead to exactly the same results as were arrived at above empirically: the former having the advantage of greater generality, the latter of being more easily comprehensible. All three methods can be employed with almost equal ease to deduce the equations for chemical equilibrium at constant temperature, *i.e.* for isothermal equilibrium. The thermodynamical method alone gives us direct information as to the excessively important influence of temperature; the molecular method allows of some conclusions being drawn, although with difficulty; and to the empirical mode there must be added a new principle to enable us to obtain information even as to the character, without speaking of the amount, of the influence of temperature.

This additional empirical principle is a special case of a law of great generality, which, it would appear, has not yet found a complete expression. The law was comparatively early, but insufficiently, formulated by Maupertuis in the first half of last century as the principle of Least Action, according to which all processes in nature take place in such a way that the smallest possible quantity of work is expended, or that the existing configurations suffer the least possible disturbance. While this principle was formerly limited to dynamical, or at most to optical applications, there is at present a growing

recognition that it is everywhere valid and can be applied to all processes whatsoever.

It may be put into the following shape:—If, in a system in equilibrium, one of the conditions of equilibrium is forcibly altered so that the system assumes a new state, then the other correlative conditions change in such a manner as to resist the alteration in the first condition.

Applied to the case before us, the principle becomes the following special law. If a system be in such a state of chemical equilibrium that any alteration of the temperature will cause a displacement of the equilibrium, *i.e.* will originate a chemical process within the system, then the displacement will always take place in such a direction that the heat of reaction serves to counteract the effect of the change of temperature. If we heat the system therefore, the reaction which takes place will be accompanied by absorption of heat; if we cool the system, the corresponding reaction will develop heat.

The simplest example of this principle is to be found in the case of simple heterogeneous equilibrium, regulated, as we have already seen (p. 251), by the formula

$$\frac{dp}{dT} = \frac{\rho}{Tu}.$$

This equation was proved for the passage of liquids into vapour, *i.e.* for a case of heterogeneous equilibrium of the first order (p. 292), the signification of the symbols being— $dp$  change of pressure,  $dT$  change of temperature,  $\rho$  heat of vaporisation,  $T$  absolute temperature of transformation,  $u$  change of volume on vaporisation. It was then shown that the equation had a wider significance. Indeed, the only assumption made in deducing it was that the pressure should be independent of the quantity of substance in one state (liquid), but dependent on the quantity in the other (gas). This assumption is equally valid for processes of dissociation such as we are considering, *e.g.* the transformation of calcium carbonate into calcium oxide and carbon dioxide, and consequently the formula is also applicable to them.

The sign of the quantity  $\rho$  is so chosen that heat absorbed on the transformation shall be reckoned positive, and heat given out, negative. In thermochemistry heats of reaction are reckoned in the opposite way: heat given out is there positive. Attention must be paid to this point of difference when the formula is being used. Heat is absorbed in the decomposition of calcium carbonate, therefore we make  $\rho$  positive in the above equation. From this it results that  $dp$  must have the same sign as  $dT$ , *i.e.* the dissociation-pressure increases with rise of temperature.

No case in which a measurable dissociation is accompanied by development of heat has as yet been thoroughly investigated. Numerous phenomena, however, are known qualitatively which were formerly considered very

enigmatical, but which are easily explained by our principle. There are compounds stable under ordinary conditions which at higher temperatures decompose into their elements with evolution of heat, while again at the very highest temperatures they exhibit a surprising degree of stability—being then even freely formed from their elements. Cyanogen and acetylene are examples. Both gases are formed in quantity at the highest temperatures we can produce—in the electric arc and in the blast-furnace; while at a red heat they cannot exist, but either fall into their elements or pass into more stable compounds (*e.g.* acetylene into benzene). These are substances for which  $\rho$  is negative, and consequently for which  $dp$  and  $dT$  have different signs, so that with rise of temperature the dissociation diminishes and the stability becomes greater.

These considerations are of great importance for the relative stability of different substances and for the possibility of the existence of stable compounds at high temperatures. We usually conceive the influence of temperature on chemical compounds to be of such a character that the higher the temperature rises the more unstable these become, until they at last fall asunder into their elements. This is quite right for compounds which are formed with evolution of heat, on whose dissociation therefore heat would be absorbed: but just the opposite holds for substances formed with absorption of heat. As has been explained, these become more stable the higher the temperature rises. It is thus by no means indubitable that in the sun's atmosphere the elements are, as some think, all present in the free state owing to the very high temperature; on the contrary, it is quite possible that various compounds exist there, of which we have as yet no knowledge whatever.

The law has another application—to solutions, namely. It is well known that some substances dissolve with evolution, others with absorption of heat. If now we have a saturated solution at a definite temperature, and heat it in presence of excess of the dissolved substance, then the equilibrium will suffer displacement so as to resist the heating. If further solution is attended by absorption of heat, such solution will occur; if, on the other hand, further solution would condition further heating, it will not take place, but there will rather be a deposition of the dissolved substance, for such deposition occasions the cooling demanded by the fundamental law.

Sodium sulphate is a good example of this. Glauber's salt,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , dissolves with considerable absorption of heat; its solubility therefore increases with rise of temperature. On the other hand, anhydrous sodium sulphate dissolves with evolution of heat, and so its solubility-curve (known above  $33^\circ$ , cf. p. 151) sinks as the temperature rises.

Attention should be paid to the fact that it is the sign of the heat of solution in the almost saturated solution which determines the sense of the change of solubility with temperature. Substances which dissolve to a large extent in water usually have their heat of solution smaller the more

concentrated the solution becomes, and it is not impossible that such substances, having a small negative heat of solution in dilute solutions, may acquire a positive heat in more concentrated solutions, so that only the sign in almost saturated solutions is of use in the application of the above principle.

The exposition just given on the basis of the equation  $\frac{dp}{dT} = \frac{\rho}{T_u}$  is true in the first instance only for the narrow group of phenomena for which the formula was developed, *i.e.* the states of heterogeneous equilibrium of the first order—between two substances only. We might inquire if an extension of the equation is not possible which would comprehend all states of equilibrium. Such an extension may in fact be made, but not in an elementary way without great difficulty. The reader must therefore rest content with an indication and exposition of the results obtained (very simply) by means of higher analysis.

In the first place, by assuming the validity of Boyle's Law and Gay-Lussac's Law for vapours, we can put the equation into the form

$$\lg p = -\frac{\rho}{2T} + C,$$

or

$$\lg \frac{p}{p_0} = \frac{\rho}{2} \left( \frac{1}{T_0} - \frac{1}{T} \right),$$

C being a new constant.

When more than one substance with variable concentration is concerned in the process, the first equation becomes

$$\lg \frac{q_1^{m_1} q_2^{n_2} q_3^{m_3} \dots}{p_1^{m_1} p_2^{m_2} p_3^{m_3} \dots} = \frac{\rho}{2T} + C.$$

Here  $p_1, p_2, p_3, \dots$  indicate the pressures exerted by the original,  $q_1, q_2, q_3, \dots$  those by the resulting substances of variable concentration. The exponents  $m_1, m_2, \dots, n_1, n_2, \dots$  denote the number of molecules of the substance in question taking part in the reaction. The equation is true for processes into which solids enter, as well as for those entirely confined to gases. In the same way it holds for both gases and dilute solutions, and thus comprehends with tolerable completeness all we know of chemical equilibrium. It must not be forgotten that it was deduced on the assumption of the validity of Boyle's and Gay-Lussac's Laws, and is consequently only applicable within the limits between which these laws are a sufficient approximation.

For example, in the case of the dissociation of phosphorus pentachloride,  $\text{PCl}_5 = \text{PCl}_3 + \text{Cl}_2$ , the equation assumes the following form—

$$\lg \frac{q_1 \cdot q_2}{p_1} = \frac{\rho}{2T} + C,$$

where  $q_1$  is the pressure of the trichloride,  $q_2$  of the chlorine, and  $p_1$

of the undecomposed pentachloride. For the dissociation of iodine vapour it is

$$\lg \frac{q^2}{p} = \frac{\rho}{2T} + C,$$

$q$  referring to the dissociated,  $p$  to the undissociated portion.

In a case investigated by Horstmann, viz. the chemical equilibrium between hydrogen, carbon dioxide, carbon monoxide, and water-vapour, when mixtures of hydrogen and carbon monoxide are exploded with insufficient quantities of oxygen, the equation is

$$\lg \frac{q_1 q_2}{p_1 p_2} = \frac{\rho}{2T} + C,$$

$p_1 p_2$  referring to the one pair, hydrogen and carbon monoxide,  $q_1 q_2$  to carbon dioxide and water-vapour. In all cases it appears that with rising temperature the equilibrium suffers displacement in the direction of the reaction in which heat is absorbed; the dissociation of phosphorus pentachloride and of iodine increases with increase of temperature; and, in the same way, more carbon dioxide is formed the higher the temperature rises, for the heat of combustion of carbon monoxide is somewhat smaller than that of hydrogen.

The law too has its application to dilute aqueous solutions. Sodium sulphate is partially decomposed by hydrochloric acid, heat being thereby absorbed. Consequently the higher the temperature is, the further does the decomposition of the sodium sulphate proceed. Van't Hoff, who was the first to make such applications of the law, found the actual process to agree closely with the theory.

The preceding thermodynamical discussion was confined exclusively to states of equilibrium; and, in fact, it is only with such states that the science at its present stage allows us to deal. We saw above (p. 298), however, that these states are the result of two opposed processes, which occasion no further change in the system when the opposite velocities have become equal. But in the equations we have been using it is always possible to replace the ratio of the active masses (concentrations or pressures) by the inverse ratio of the corresponding velocities, so that we obtain

$$\lg \frac{c}{c_1} = \frac{\rho}{2T} + C.$$

It is true that from this formula we can learn nothing of the separate velocities  $c$  and  $c_1$ , but still we can see how their ratio varies with the temperature. If  $\rho = 0$ , *i.e.* if the reaction takes place without thermal effect, then  $c : c_1$  does not alter, and so we conclude that the velocities of the opposed actions alter in the same proportion for any given change of temperature. If  $\rho$  has a finite value, the velocity of the reaction taking place with absorption of heat will increase more rapidly with rise of temperature than that of the other, so that in

accordance with our principle the equilibrium will be displaced in favour of the first reaction.

As to the form of the equation representing the influence of temperature on the velocity of reaction, we can only conclude that the factors of other functions of  $T$  occurring in the equation must be equal, as they destroy each other in the quotient. This too is quite plausible ; for the opposed reactions take place under exactly the same conditions in one and the same system.

## CHAPTER V

### APPLICATION OF THE KINETIC MOLECULAR THEORY TO CHEMICAL EQUILIBRIUM

IN the preceding chapter attention was called to the possibility of obtaining the formulæ for chemical equilibrium on the basis of the molecular theory. The considerations here involved teach us little or nothing new; but they at least give us, instead of a mere abstract formulation of the results, a clear idea of how the equilibrium comes about.

We already know how to conceive a chemical process in the light of this theory. The atoms of the reacting substances come into close contact with each other, and, it may be, part in quite a different way, the atoms formerly separate remaining united, and *vice versa*. This takes place excessively often, for even such apparently simple processes as the formation of hydrochloric acid are cases of double decomposition, as appears from the equation  $\text{H}_2 + \text{Cl}_2 = 2\text{HCl}$ .

Chemical processes in general require time for their completion. Now, reasoning *à priori*, it is difficult to see, if the conditions exist for some molecules reacting, why all the others should not at the same time do likewise. If we mix acetic acid and alcohol at the ordinary temperature, small quantities of acetic ether are formed after a few seconds; yet in order that as much of the ether can be produced as is possible under the existing circumstances, years—strictly speaking, an infinite time—must elapse.

The explanation of this apparent contradiction was given by Pfaunder (1867), the fundamental idea having already been stated for a limited number of cases by Williamson (1851) and Clausius (1857). It lies in the recognition that the state of the molecules in a homogeneous system at a constant temperature is by no means everywhere the same; but that some of the molecules regularly diverge more or less widely from the average state. A process can thus begin when only a few of the molecules are in the requisite state of motion or vibration, and for the completion of the process it is necessary that



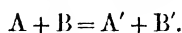
all the molecules, in assuming all conceivable states between the possible limits, should once enter into that state, or range of states, in which they are capable of reacting in the required way. To come back to our former example—there are only relatively few molecules of acetic acid and alcohol in a position to react so as to form acetic ether and water; when the process between them is completed, a further reaction can take place only when other molecules have assumed the proper state.

It is manifest that the chemical process will proceed faster the more molecules there are in the active state and the oftener they meet; the latter circumstance depends again on the number of the molecules in the space, and the velocity these possess. The conditions become in general more favourable with rise of temperature; the velocity of translation, and consequently the frequency of encounter increases, while the coherence of the molecule is diminished in consequence of the more frequent and more energetic collisions, so that it becomes more capable of reacting.

On this basis we can evolve a theory of the action of mass which yields the same formulæ as we found above. The following considerations were published by Guldberg and Waage (1879), and present the reason for the laws in the clear manner peculiar to the molecular theory.

“If we consider a chemical process taking place under such circumstances that two substances A and B are converted into two others A' and B', while at the same time the reconversion of A' and B' into the original A and B can also occur, then the mere assumption of attractive forces between the substances or their components is no longer sufficient to explain the reactions, but we must for this purpose take account of the motion of the atoms and molecules.

“The equilibrium between two such chemical processes is a mobile equilibrium, for two opposite reactions take place simultaneously—fresh quantities of A' and B' being formed while A and B themselves are being reproduced. When equal quantities of these pairs are formed in unit time, equilibrium results. The chemical reaction for the conversion of A and B into A' and B' is represented by the equation



“If the molecule A is composed of the atoms or molecules  $\alpha$  and  $\gamma$ , these latter execute their own proper movements within the compound molecules. Owing to these proper movements,  $\alpha$  and  $\gamma$  will now approach, now retire from each other, and under certain circumstances their motions will become of such extent as to decompose the molecule A into the two components  $\alpha$  and  $\gamma$ . The same holds for  $\beta$  and  $\delta$ , the components of the molecule B. Now, as each of the compound molecules A and B is in motion as a whole, it will from time to time come to pass that a molecule A will encounter a molecule B. If this encounter of A and B happen under such circumstances that either  $\alpha$  and  $\gamma$  as well as  $\beta$  and  $\delta$  are completely separated from each

other, or at least that the distance between  $\alpha$  and  $\gamma$  on the one hand, and between  $\beta$  and  $\delta$  on the other, has almost reached the boundary of the sphere of action, then the chemical forces of attraction between  $\beta$  and  $\gamma$ , and between  $\alpha$  and  $\delta$  can do no other than condition the formation of two new molecules  $A'$  and  $B'$ , where  $A' = \alpha + \delta$  and  $B' = \beta + \gamma$ . In the same way an encounter of two molecules  $A'$  and  $B'$  may cause the formation of  $A$  and  $B$ , if the components  $\alpha$  and  $\delta$ , on the one hand, and  $\beta$  and  $\gamma$ , on the other, are either completely separated or so far removed from each other that the attractive forces between  $\alpha$  and  $\gamma$  and between  $\beta$  and  $\delta$  are capable of effecting the formation of new molecules  $A = \alpha + \gamma$  and  $B = \beta + \delta$ .

"When we are dealing with an addition instead of a double substitution similar considerations are to be employed. A compound molecule  $ABC$  can, under certain conditions, fall into its components  $A$ ,  $B$ , and  $C$ , while simultaneously, by the encounters of the molecules  $A$ ,  $B$ , and  $C$ , new molecules of the formula  $ABC$  can be formed.

"The rate of formation of new substances may be determined in the following way. If the number of molecules of  $A$  and  $B$  in unit volume be denoted by  $p$  and  $q$ , the product  $pq$  will represent the frequency of the encounters of these molecules. If now each motion of the various molecules be equally favourable to the formation of new substances, the velocity of the chemical reaction— in other words the quantity transformed in unit time—may be made equal to  $\phi pq$ , the coefficient of velocity being supposed dependent on the temperature.

"This view, already known from the theory of gaseous dissociation, may now be extended as follows so as to become generally applicable to all states of aggregation.

"Amongst the  $p$  molecules of  $A$  in unit volume, there will be in general only a certain fraction of them,  $a$ , in such a condition that on encounter with the molecules of  $B$  a chemical exchange will take place. Similarly, amongst the  $q$  molecules of  $B$  contained in unit volume, there will only be a fraction  $b$  in the state requisite for chemical exchange with the molecules of  $A$ . Thus on the whole there are in unit volume  $ap$  molecules of  $A$  and  $bq$  molecules of  $B$ , which on meeting will be transformed into new substances. Consequently the frequency of encounter of the active molecules will be represented by the product  $ap \cdot bq$ , and the rate at which the formation of new substances will proceed is to be expressed thus

$$\phi ap \cdot bq = kpq,$$

if for brevity we put  $\phi ab = k$ .

"A still further extension is possible, so that all reactions may be included, irrespective of the number of substances taking part in them. If, for example, the formation of new compounds is rendered possible only by the encounter of three different substances  $A$ ,  $B$ , and  $C$ ; and if the number of molecules of these in unit volume be respectively,  $p$ ,  $q$ , and  $r$ ;  $a$ ,  $b$ , and  $c$ , lastly, being the coefficients peculiar to the substances—then we get as the expression for the velocity

$$\phi ap \cdot bq \cdot cr = kpqr,$$

$k$  again representing the product of the coefficients.

"The rate of formation of an addition compound  $\alpha A + \beta B + \gamma C$ , com-

posed of  $\alpha$  molecules of A,  $\beta$  of B, and  $\gamma$  of C, will be expressed by

$$\phi \cdot \text{ap} \cdot \text{ap} \dots \text{bq} \cdot \text{bq} \dots \text{cr} \cdot \text{cr} \dots = \phi(\text{ap})^\alpha (\text{bq})^\beta (\text{cr})^\gamma = k p^\alpha q^\beta r^\gamma,$$

where  $k$  denotes the product of the coefficients.

"Both the coefficient of velocity and the coefficients  $a$ ,  $b$ ,  $c$ , characteristic of the substances, must be supposed to be dependent on the temperature. The nature of this dependence can be ascertained only by experiment.

"If the velocity of formation of the new substances is in this way determined, we need only in order to obtain the condition for equilibrium equate the velocities of the two opposed reactions.

"If we wish to determine the absolute velocity of the chemical process, we can easily see that this must be equal to the difference of the opposite velocities of reaction."

On this basis we can without further assumptions develop all cases of homogeneous equilibrium, inclusive of dissociation, as Guldberg and Waage show in the course of their paper. As, however, the separate applications have already been discussed in detail in the previous chapters, they need not be here deduced anew.

One difficulty of a peculiar nature has stood in the way of the application of the kinetic hypothesis to heterogeneous equilibrium. It appears, namely, at the first glance—and this conclusion has often been openly expressed—as if the equilibrium cannot be independent of the quantity of the solid substance present, although this is actually the case. Take, for instance, the dissociation of calcium carbonate. A state of equilibrium will be assumed when from the surface of the calcium carbonate as many particles of carbon dioxide are given off as are taken up in the same time by the surface of calcium oxide. From this it seems directly to follow that the equilibrium depends on the ratio of the surfaces of the carbonate and the oxide, which is contrary to experience.

This apparent contradiction caused Horstmann to declare the kinetic hypothesis, interpreted as above by Pfaundler, to be incorrect; Pfaundler on his side indicated that the experimental result could be deduced from the kinetic theory, but nowhere to the author's knowledge has he published this deduction.

Now, *à priori* it must appear probable that the kinetic theory, which in its consequences has been so often found in harmony with experience, can scarcely fail in this case to be so again if only it be properly applied. In the author's opinion the want of agreement is caused by the consideration of the matter not having been sufficiently thoroughgoing.

Let us in the first place consider a case of heterogeneous equilibrium in which a solid or liquid passes completely into a gas, or a solid completely into a liquid. As a concrete example we may take the equilibrium between paracyanogen and cyanogen, or between a salt and its saturated solution. Let us keep in view a small portion of the

surface of the solid and the quantity of the gas or liquid in its immediate neighbourhood; there will be equilibrium between these when the same number of molecules enter and leave the bounding surface. This evidently also holds good for every part of the surface of the solid (and consequently for the whole surface), each being considered along with the neighbouring portion of the gas or liquid.

The interior of the solid has no influence on the equilibrium, for as the solid passes into the other state of aggregation without residue, no alteration of the surface can be brought about by the dissociation, and so it is all one whether new portions of the solid come to the surface or not.

It is further required that the layer of gas or liquid next to the one in contact with the solid should be in equilibrium with this latter layer; which is obviously the case when the concentration of the gas or the solution is the same in the two. So long as this is not attained, the separated molecules migrate to the more distant parts of the space in virtue of difference of pressure or by diffusion, until finally the whole volume, irrespective of its size, is uniformly filled by the gas or by the dissolved substance. In this way we arrive at the result, agreeing with experience, that the equilibrium is conditioned only by the density of the gas or the concentration of the solution—in a word, by the active mass. Since, with rise of temperature, the molecules, in consequence of their brisker motion, are more easily broken off and more difficult to retain, the decomposition must increase with increase of temperature.

Considerations of a similar nature lead us also to the comprehension of the equilibrium between several solids and one or more gases, under which head fall the decomposition of calcium carbonate, the dehydration of hydrated salts, etc. At first sight the conclusion that the relative quantities of the solids are of influence on the equilibrium seems inevitable, but a somewhat deeper analysis shows that this case is precisely similar to that just considered.

Let us imagine a piece of calcium carbonate enclosed in a close-fitting air-tight shell at a temperature at which certain molecules of carbon dioxide, whose kinetic energy exceeds the average by a certain amount, could just break loose from the solid. They do not do so, however, for there is no space into which they can go. We have such a case when the carbonate is placed over liquid metal in a tube closed at the upper end.

Let us pump a portion of the metal out, so that a vacuum is produced. Immediately molecules of carbonic acid fly off from the carbonate, whose surface then becomes covered with a molecular layer of oxide. But this layer is not in stable equilibrium either with the neighbouring gas or with the layer of carbonate immediately under it. For the superficial layer of the solid being in general very small compared to the free space above it, only relatively few molecules of carbon dioxide will at first leave the extreme surface, and as a portion of them fly back, some will be retained; thus

there will result a temporary state of equilibrium lying far beneath the stationary equilibrium of dissociation.

This state will now be disturbed by the layer of carbonate lying immediately under that of the oxide. In this layer also there is a definite proportion of the molecules above the temperature for decomposition, and molecules of carbon dioxide continually separate, to enter the superposed layer of calcium oxide, and there in the first instance to be held fast. Soon, however, the new superficial molecules of carbonate begin to dissociate; fresh molecules of carbon dioxide enter the gas, and a new transitory equilibrium is established—a state coming nearer the stationary equilibrium than the first did.

The same series of processes is repeated with the deeper layers of the carbonate, and now we have to ask when and how a stationary state will be reached. Between the undecomposed carbonate and the gas there is formed by the processes described a layer of partially decomposed carbonate, and equilibrium will be attained when at the two limiting surfaces of this intermediate layer, the ratio of the carbonic acid molecules entering and leaving shall have assumed the same constant value. This ratio is given by the ratio of the number of molecules of carbonate above the temperature of decomposition to the number below the temperature of decomposition. The state of the intermediate layer is regulated by this ratio, and as the same condition holds for every part of the gas—that through any surface equal numbers of molecules pass in and out in a given time—it follows that the intermediate layer behaves as a portion of the space occupied by the gas. Thus we have reduced this case to the former, in which the solid passed completely into gas; and the considerations given there, from which we concluded that the stationary state is independent of the size of the free space and also of the relative quantity of the solid, are equally applicable to the process under discussion.

It should be particularly remarked that the compact masses in the interior of a calespar crystal, although they could decompose, do not in fact do so, on account of there being no space into which the molecules of carbonic acid can move. The phenomena of dissociation take place exclusively at the limiting surfaces of the intermediate layer. As this must be thicker the smaller the surface of the solid is in comparison to the free space, and as the movement of the dissociated gas-molecules through it must be comparatively slow, it follows that equilibrium will take the longer to be reached, the less surface the solid presents. Experience abundantly confirms this.

How these considerations may be applied to other similar cases need not be specially shown. The essential thing to be remembered is the part played by the surface separating the different aggregates in contact with one another.

# BOOK XI

## CHEMICAL AFFINITY

### CHAPTER I

#### EXPERIMENTAL METHODS

IN dynamics the magnitude of a force is defined and measured by the change of velocity it imparts to a definite mass in a definite time. A second mode of measuring forces consists in the establishment of equilibrium between the given force and one oppositely directed of known or ascertainable magnitude; this is really a special case of the first general mode, the change of velocity consequent on the application of the given force being reduced to nil by an equal and opposite force. The second method, although thus derivative, possesses all those essential advantages over the general one which are peculiar to such zero-methods, and is therefore far more frequently employed.

The measurement of the intensity of chemical forces can likewise be undertaken according to two methods, quite analogous to those of general dynamics. The more usual, for experimental reasons, is the static method, in which a chemical process is limited in definite proportions by a process oppositely directed, *i.e.* one that reproduces the original substances from the products of the direct process. Parallel to the kinetic method, we have that which obtains a measure of the active forces from the velocity of a chemical process. The two chemical methods are connected with each other in the same way as the two dynamical methods; for, as has been already fully explained (p. 298), we may look upon the equilibrium of chemical processes as resulting from the mutual cancelling of two numerically equal but oppositely directed chemical processes.

The experimental proof of this intimate connection required by the theory between the velocities of opposite reactions and the quantitative relations of mass for which chemical equilibrium appears, can only in the

first instance be given for processes in which both can be measured. The formation of the esters from acids and alcohols and their decomposition by water, seems to be the most suitable for this purpose, and although it did not occur to Berthelot and Péan de St. Gilles to make such an application of their experiments, there are amongst these several that apparently might be utilised. Nevertheless, the possibility of an exact comparison is excluded on account of equivalent quantities of ester and water not forming a homogeneous mixture. The active masses are thereby altered, and from the experiments we can only learn that, corresponding to expectation, the formation of ester from acid and alcohol proceeds much more rapidly than its decomposition by the action of water. It has been recently shown, however, in another way to be discussed later, that the connection in question actually does exist.

From the measurement of the velocities of chemical reactions we are enabled to solve the old problem of measuring the intensity of chemical forces. If two analogous substances (*e.g.* two acids) occasion under the same conditions analogous processes with different velocities, we shall attribute greater intensity of the chemical forces to the substance generating the greater velocity. And similarly of two acids competing for the same base, we shall call that the stronger which after equilibrium is established has neutralised the larger quantity of the base.

I should like to call attention at this point to a possible error, which has indeed on occasion been committed. The words velocity and force in their application to chemical processes have not their ordinary dynamical significance, but are employed in a merely figurative sense. Chemical velocity is not the ratio of a space passed over to the corresponding time occupied, but the ratio of a quantity of substance transformed to the time required for the transformation; in other words, ordinary velocity is rate of motion, chemical velocity is rate of material transformation. Similarly, chemical force is not the cause of motion, but of chemical transformation. We can therefore by no means directly apply dynamical theorems concerning ordinary forces and velocities to chemical phenomena. It is true, as has just been shown, that certain similarities do exist, but along with them exist also important differences.

The chief example of such differences is that a single impulsive action of force does not produce, as in dynamics, a permanent (uniform) motion. A chemical process only lasts as long as the chemical force is in action, being at each instant proportional to it. If we want a dynamical analogy therefore, we must seek it in the motion of a body in a fluid of great viscosity.

According to the general relations just explained, the methods for the determination of the constants of chemical processes fall into two groups,—the kinetic or velocity-methods, and the static or equilibrium-methods. We shall begin with the last, as they are older in their

application, and, containing one variable less (time), are to a certain extent simpler than the first.

To ascertain the proportions of the active masses in a case of chemical equilibrium we proceed in two ways, which may be designated shortly, but not very aptly, by the terms chemical and physical. The methods are mostly employed separately, but sometimes together. The chemical method is applied to heterogeneous equilibrium. A separation of the different portions and a chemical analysis of the separated substances is here possible, the analysis usually giving directly the numbers required. Several examples of this have already been given in the discussion of heterogeneous equilibrium (p. 299).

The physical methods are chiefly employed in cases of homogeneous equilibrium, where a mechanical separation of the components is not practicable, and chemical analysis gives us no information as to the magnitudes sought. They rest on the principle that conclusions as to chemical processes or states of distribution may be drawn from the measurement of accompanying physical processes, or of physical properties depending on the chemical distribution. The theory of these methods was first given by Steinheil (1843), and later (in 1848) R. Hofmann, at Kirchhoff's instigation, developed it in a similar way.

In general, every physical property which is retained unaltered by the elements of a compound, whether separate or united, and for the measurement of which, instruments of sufficient accuracy to keep the errors of observation within proper limits can be constructed, may be used as a means of quantitative analysis.

The physical methods in the principal case of aqueous solutions take the following form. Let any property that can be represented as a sum of separate terms, of which each is proportional to the quantity of one of the substances present, have the value  $A$  for a mixture of the reacting substances. If the quantities of these be  $p$ ,  $q$ ,  $p'$ , and  $q'$ —to use the same letters as before,—and if  $\alpha$ ,  $\beta$ ,  $\alpha'$ , and  $\beta'$  be the coefficients of proportionality of the corresponding substances with respect to the property in question, we have the equation

$$A = \alpha p + \beta q + \alpha' p' + \beta' q'.$$

Now let a reaction take place, the quantity  $\xi$  of  $p$  and  $q$  disappearing, and the same quantity of  $p'$  and  $q'$  being produced. The property will then assume a new value  $A'$ , corresponding to the formula

$$A' = \alpha(p - \xi) + \beta(q - \xi) + \alpha'(p' + \xi) + \beta'(q' + \xi),$$

whence

$$\xi = \frac{A - A'}{\alpha + \beta - (\alpha' + \beta')}.$$

In this way the distribution of the substances in the solution can be determined, if the four coefficients  $\alpha$ ,  $\beta$ ,  $\alpha'$ ,  $\beta'$  and the total value of the property before and after the reaction are known.

The method unfortunately loses its applicability to a case con-



stantly occurring. This case is characterised by the relation between the coefficients  $a + \beta = a' + \beta'$  or  $a + \beta - a' - \beta' = 0$ . Then the denominator of the fraction  $\xi = \frac{A - A'}{a + \beta - (a' + \beta')}$  is equal to zero, and as  $A - A' = \xi(a + \beta - a' - \beta')$ , we have also  $A - A' = 0$ , so that the expression for  $\xi$  takes the indeterminate form  $\frac{0}{0}$ . The property  $A$  retains its value for all values of  $\xi$ , so that  $\xi$  cannot be determined.

This critical case almost always appears when  $M, N, M', N'$  are all analogous binary substances, such as neutral salts or esters. For many properties of such substances the horizontal and vertical differences are constant in the table we have often used—

$f(a + b)$	$f(a + b')$	$f(a + b'')$	...
$f(a' + b)$	$f(a' + b')$	$f(a' + b'')$	...
$f(a'' + b)$	$f(a'' + b')$	$f(a'' + b'')$	...

Here  $aa' \dots bb' \dots$  are the components, and  $f(a + b) \dots$  represents the properties of the compounds in question. We have, for example,  $f(a + b) - f(a + b') = f(a' + b) - f(a' + b')$ . As the substances,  $M$  and  $N$  can transform themselves into  $M'$  and  $N'$ , the coefficients have the following values:— $a = f(a + b)$ ,  $\beta = f(a' + b)$ ,  $a' = f(a + b')$ ,  $\beta' = f(a' + b')$ . The relation just established gives therefore  $a - a' = \beta' - \beta$ , or  $a + \beta - a' - \beta' = 0$ , which is the critical case.

We do not even need this algebraical proof to see the inapplicability of the method under the given conditions. The whole significance of the law of constant differences in properties is contained in the fact of these properties depending only on the nature of the components and not on their distribution. If therefore the distribution is of no influence on the property, it is evident that from measurements of the property no conclusions whatever can be drawn as to the distribution.

Gladstone was the first to apply physical methods in a systematic manner to the solution of problems of affinity. From his researches we can at once see the multiplicity of forms that can be assumed by the physical methods according to circumstances. Besides change of colour, which he employed by preference, he turned to account fluorescence, circular polarisation, and the phenomena of diffusion for the same purpose. The quantitative development of the method, however, was only partially carried out by him, for, since he had no theory of the phenomena he was investigating, no great interest was attached to them.

An example of the physical method in a fully developed form is first found in Julius Thomsen's calorimetric researches (1869), which yielded all necessary information as to the distribution of substances in a homogeneous liquid.

The coefficients  $\alpha$ ,  $\beta$ ,  $\alpha'$ ,  $\beta'$ , are here simply quantities of energy. If we deal, for example, with the action between sodium fluoride and hydrogen chloride, hydrogen fluoride and sodium chloride being formed, we have

$\alpha$	the energy of 1 equivalent of sodium fluoride,
$\beta$	hydrochloric acid,
$\alpha'$	sodium chloride,
$\beta'$	hydrofluoric acid.

In the equation

$$\xi = \frac{\Lambda - \Lambda'}{\alpha + \beta - (\alpha' + \beta')}$$

$\Lambda$  denotes the energy of the initial state,  $\Lambda'$  the energy of the state of equilibrium;  $\Lambda - \Lambda'$  is consequently the thermal effect of the action of hydrochloric acid on sodium fluoride. The denominator is the difference of energy between sodium fluoride plus hydrochloric acid, and sodium chloride plus hydrofluoric acid, *i.e.* the thermal effect of the total transformation of the two first substances into the two last. To ascertain this, it is necessary to split up sodium fluoride into soda and hydrofluoric acid, and then neutralise the former with hydrochloric acid; the magnitude in question is therefore merely the difference of the heats of neutralisation of the two acids.

Now the heat of neutralisation of hydrofluoric acid is 162.7 K, and of hydrochloric acid 137.4 K; the difference is 25.3 K, so we have  $\alpha + \beta - (\alpha' + \beta') = -25.3$  K. On the other hand, when 1 eq. of hydrochloric acid acts on 1 eq. of sodium fluoride there is observed a heat-absorption of -23.6 K. Substituting these values, we obtain

$$\xi = \frac{-23.6}{-25.3} = .933.$$

In this process therefore .933 of the equivalent or 93.3 per cent of the hydrofluoric acid is liberated by the hydrochloric acid.

We have, in arriving at this result, made the tacit assumption that no other alteration of energy takes place beyond that occasioned by the double decomposition. Now this supposition is not always correct; the substances present often act in quite another direction also, so that corresponding corrections must be applied. This is done by determining the thermal value of the secondary reactions from special experiments and deducting it from the difference  $\Lambda - \Lambda'$ . The formula is then

$$\xi = \frac{\Lambda - \Lambda' - q}{\alpha + \beta - (\alpha' + \beta')}$$

In many cases there is encountered the difficulty that  $q$  itself is a function of the value  $\xi$  to be determined. It is then simplest to calculate the values  $\Lambda'$  and  $q$  for some arbitrary values of  $\xi$ , which

are so to be chosen that the real value of  $\xi$  falls amongst them, and so can be calculated with sufficient accuracy by interpolation.

The determination of the heat of neutralisation is rendered more difficult if the bases to be investigated are insoluble. Since, however, the heats of neutralisation themselves are not required to determine the ratios of distribution, but only their differences, we can avoid the direct determination by using the following theorem.

The difference between the heats of neutralisation of two acids  $A_1$  and  $A_2$  with the same base  $B$ , is equal to the difference between the thermal effects of the action of  $A_1$  on the salt  $A_2B$  and of  $A_2$  on the salt  $A_1B$ .

The theorem may be easily proved by means of the corresponding energy-equations. Let there be produced when  $A_1$  acts on  $A_2B$  the quantity  $\xi$  of  $A_2$  and the same amount of  $A_1B$ ; the corresponding thermal effect  $Q_1$  has the value given by the equation

$$A_1 + A_2B = (1 - \xi)A_1 + (1 - \xi)A_2B + \xi A_2 + \xi A_1B + Q_1.$$

In the reverse action the same final state is reached, for the same components are present in the same proportions; the energy-equation is therefore

$$A_2 + A_1B = \xi A_2 + \xi A_1B + (1 - \xi)A_1 + (1 - \xi)A_2B + Q_2.$$

Subtracting, we get

$$A_1 + A_2B - A_2 - A_1B = Q_1 - Q_2.$$

Again, the heats of neutralisation  $W_1$  and  $W_2$  are given by the equations

$$\begin{aligned} A_1 + B &= A_1B + W_1 \\ A_2 + B &= A_2B + W_2. \end{aligned}$$

Subtraction gives

$$A_1 - A_2 - A_1B + A_2B = W_1 - W_2,$$

and by comparison with the above difference,

$$Q_1 - Q_2 = W_1 - W_2,$$

which was to be shown.

The formula holds good whether there are secondary reactions or not, for these influence the right sides of the equation containing  $Q_1$  and  $Q_2$  in exactly the same way, so that they disappear on subtraction.

Thomsen has proved from special experiments on soluble bases that the differences determined directly are identical with those determined indirectly. This result justifies the assumption made above that the same final state is reached in the two opposite reactions.

A process in applicability equal to the calorimetric method, but much easier and more convenient in the performance, is the volumetric method based on the determination of the specific volume. The utilisation of the specific gravity for the quantitative estimation of dissolved substances reaches back to antiquity, and to-day occupies an important place both in the arts and in science. It is therefore surprising that the application of this method to the determination of

the distribution of substances in homogeneous solutions was so long delayed. The first experiments were made by Tissier in 1859.

Ostwald afterwards (1878) made numerous measurements by this method on the distribution of different bases between pairs of acids acting simultaneously. We shall content ourselves here with a general description of the method; the results obtained will be given later.

If  $d$  is the specific gravity of a liquid, then  $\frac{1}{d}$  is its specific volume, *i.e.* the volume occupied by unit weight. Multiplying this by the weight of the solution containing one gram-molecule of the substance considered, we obtain the molecular volume of the solution. If we bring together different solutions that can act chemically on each other, and so let the process take place, the molecular volume of the mixed solution is seen to be different from the sum of the volumes of the components.

The alteration of the molecular volume on neutralisation is proportionally much greater and much more varied than is the case with the corresponding heats of neutralisation, so that the critical case, in which the method gives no result, occurs much less frequently than with the calorimetric method. The underlying principle, however, is in no way different, and the formula

$$\xi = \frac{\Lambda - \Lambda'}{a + \beta - (a' + \beta')}$$

still holds good, the separate letters having merely a correspondingly altered signification.  $\beta' - a$  and  $\beta - a'$  are no longer the heats of neutralisation, but the changes of volume on neutralisation, while  $\Lambda - \Lambda'$  is the change of volume occasioned by the action of the one acid on the neutral salt of the other. If secondary actions take place, we get the corrected formula

$$\xi = \frac{\Lambda - \Lambda' - q}{a + \beta - (a' + \beta')}$$

$q$  being the change of volume consequent on the secondary reactions.

The actual carrying out of the experiments can easily be brought to a high degree of accuracy by the use of the Sprengel pyknometer. The procedure is the same as in ordinary determinations of density; the temperature must be carefully kept constant, and if the pyknometer be capable of containing 20-30 g., the error is only a few units in the fifth decimal place. The solutions, of course, must be of accurately determined strengths. Ostwald prepared them in such a manner, that one gram-equivalent of each acid or base was contained in a kilogram of the solution, whereby the conversion of the specific volume into the molecular volume was rendered very simple. Of course we can also prepare solutions corresponding to a given formula, as Thomsen does in his calorimetric experiments.

To take an example—the specific volume of a potash solution, containing  $\text{KOH} = 56.1$  g. in a kilogram, was found equal to  $.950668$ ; that of a corresponding nitric acid solution equal to  $.966623$ ; the molecular volumes are  $950.668$ , and  $966.623$  c. cm. After mixture of equal weights of the two solutions, the specific volume of the potassium nitrate solution obtained was  $.968669$ ; the molecular volume (there being now  $2000$  g. of solution) is therefore  $1937.338$  c. cm., while the sum of the molecular volumes of acid and base is only  $1917.291$ . Consequently on neutralisation there is an expansion of  $20.047$  c. cm.

For the case of insoluble bases we have a theorem exactly the same as the corresponding thermochemical principle, if we substitute in the latter “change of volume” for “thermal effect.” The proof too is the same, for volumes may be added and subtracted just as quantities of energy. As fewer experiments are necessary here than in the direct determination of change of volume on neutralisation, we have reason to prefer this method in all cases.

The same difference, finally, can be ascertained in still another way, one which has no analogue in thermochemistry, on account of our inability to determine the absolute values of quantities of energy. The theorem is this—

If we subtract the molecular volumes of the two acids from the molecular volumes of the two salts, the difference of the remainders is equal to the difference of the changes of volume on neutralisation.

Let us denote the volumes of the salt-solutions by  $(A_1B)$  and  $(A_2B)$ , those of the acids by  $(A_1)$  and  $(A_2)$ , and the unknown volume of the (actually or hypothetically) dissolved base by  $(B)$ ; then

$$\begin{aligned}(A_1B) &= (A_1) + (B) + W_1 \\ (A_2B) &= (A_2) + (B) + W_2,\end{aligned}$$

where  $W_1$  and  $W_2$  are the changes of volume on neutralisation, the volume of the salt-solution being evidently equal to the sum of the volumes of the acid and base plus the change of volume on neutralisation.\* Subtracting, we get

$$(A_1B) - A_1 - \{(A_2B) - A_2\} = W_1 - W_2,$$

which proves the theorem.

Practically this principle is of little use, for we must in addition determine the volume of the mixed solution containing both acids, and thus save nothing. On the other hand, the relation is so far of importance that it allows us to judge if the composition of the solutions is accurate; for otherwise the differences determined by the two methods will not agree.

To obtain an example of the application of these two principles, we shall consider the measurements on the relative affinity of nitric and sulphuric acids for cupric oxide. The following molecular volumes were found—

\* It is assumed that exactly as much water is contained in the solution of the salt as in the solutions of the acid and base together.

1. $\text{Cu}(\text{NO}_3)_2$	3847.4
2. $\text{CuSO}_4$	3840.3
3. $(\text{HNO}_3)_2$	1933.2
4. $\text{H}_2\text{SO}_4$	1936.8
5. $\text{Cu}(\text{NO}_3)_2, \text{H}_2\text{SO}_4$	5780.8
6. $\text{CuSO}_4, (\text{HNO}_3)_2$	5781.3

From the equality of 5. and 6. it appears, firstly, that the solutions were of the proper composition; and secondly, that the final distribution is the same, independent of the original arrangement. For the values of  $Q_1$  and  $Q_2$  we must subtract 6. from the sum 2. + 3. and 5. from 1. + 4., and consequently obtain  $Q_1 = 7.8$ , and  $Q_2 = -3.4$ ; the difference is  $Q_1 - Q_2 = 11.2$ . According to the second theorem this ought to be the same as  $(1. - 3.) - (2. - 4.)$ : we find for this 10.7—a sufficient approximation.

As secondary reactions we have that of sulphuric acid on the sulphate, which is considerable, and that of nitric acid on the nitrate, which is very small; their sum is 1.2.\* We therefore have

$$\xi = \frac{7.8 - 1.2}{11.2} = .59,$$

*i.e.* nitric acid decomposes copper sulphate so that 59 per cent of the sulphuric acid is liberated, 41 per cent of the nitric acid remaining free.

The volumetric method can easily be extended to higher and lower temperatures, an extension attended by considerable difficulty in the case of the calorimetric method. We have only to determine the expansion by heat of the liquids whose volumes are to be compared, in order to acquire the material necessary for calculating the distribution of the base between the acids for every other temperature. For details of such expansion experiments the original memoirs must be consulted. It should only be mentioned that it is convenient to refer the observations to a few definite temperatures, either by maintaining these constant with the help of a thermostat, or by making observations in their immediate neighbourhood, both above and below, and then interpolating for the temperatures required. By this mode of proceeding we save the laborious calculation of interpolation-formulae, which, quite apart from the waste of time involved, always diminish the accuracy of the results. Ostwald (1877) has given an example of this process, the special results of which will be discussed at another place. The accuracy of these experiments is the same as that of density determinations with a Sprengel pyknometer, the error being a few units in the fifth decimal place.

We learned in Part I. that the specific refractive power  $\frac{n-1}{d}$  (where  $n$  is the index of refraction and  $d$  the density) is almost entirely dependent on the chemical nature of a substance, and not on the arrangement of its components. Now, as it has just been shown that

\* The separate numbers for the secondary reactions and the details of the approximate calculation are omitted, in order to save space.

the density of solutions can be applied to determine the distribution within them, it follows that the refractive index minus 1, which is proportional to the density, must be equally applicable.

This method of physical analysis was actually employed by Steinheil, and can be very well applied to the distribution of a base between two acids, the results obtained showing, as was to be expected, exactly similar relations to those observed with change of volume.

With regard to the mode of measurement, such determinations may be made with great accuracy by the use of the spectrometer; the chief difficulty is to maintain a constant temperature. The calculation of the experiments may be performed so that the observed refractive indices minus that of water are considered variable; on neutralisation, for example, the sum of these differences for the acid and base is compared to double the difference for the resulting salt-solution. It is simpler, however, to perform the calculation with the refractive indices themselves, the result being the same. It is true that so long as we consider the refractive index to be the ratio of two sines such a calculation is meaningless; but if we consider it as the numerical value of the time required by light to pass through a given distance in the liquid under investigation, the corresponding time for a vacuum (or normal air) being 1, then the addition of the indices has a reasonable meaning; for we compare the time the light requires to pass through the solutions of the acid and base in succession, with the time occupied when the acid and base are no longer separate but chemically united.

This view, based on the passage of light through equal spaces, requires that equivalent quantities of the different substances shall be present in equal volumes of the solutions, which must therefore be prepared as in chemical volumetric analysis. With solutions containing equivalents in equal weights it would be better to use the reciprocals of the refractive indices.

As an example we may take the neutralisation of potash with nitric acid. The refractive index of normal potash solution is 1·34357, of normal nitric acid 1·34076. On mixing them in equal volumes, we obtain a potassium nitrate solution whose refractive index is 1·33768. Thus we have—

Potash	= 1·34357
Nitric acid	= 1·34076
	2·68433
Potassium nitrate, $1·33768 \times 2$	= 2·67536
	Difference = ·00897

The number ·00897 is quite as characteristic of the combination of nitric acid with potash as the heat of neutralisation or the change of volume, and if different values are found for two acids, the distribution of a base between them may be ascertained just as before, the formulæ remaining exactly the same.

The optical method has the advantage over the volumetric method that it can be used with very small quantities of substance ; a few cubic centimetres are enough for a determination. On the other hand, it is less exact, for although the refractive indices themselves can be determined with extreme accuracy, yet their variations, with which alone we have to deal, are so small that the error of experiment with a spectrometer accurate to  $\pm 5''$  is still some five times greater than the error of the volumetric method.

Another means of utilising light for physical analysis is offered by photometry. The method is founded on the principle that the amount of light absorbed from a ray passing through any medium is a function of the thickness, or also of the density, of the latter. Imagine a quantity of light  $I_0$  sent into the medium, then, according to the laws of photometry, a definite fraction  $a$  is absorbed by a very thin layer. The remainder loses in the next equal layer the same fraction of its amount, and so on. We have consequently the following series :—

Layer.	Absorbed.	Transmitted.
0—1	$aI_0$	$(1-a)I_0$
1—2	$(1-a)aI_0$	$(1-a)I_0 - (1-a)aI_0 = (1-a)^2I_0$
2—3	$(1-a)^2aI_0$	$(1-a)^2I_0 - (1-a)^2aI_0 = (1-a)^3I_0$
3—4	$(1-a)^3aI_0$	$(1-a)^3I_0 - (1-a)^3aI_0 = (1-a)^4I_0$

etc.

The light,  $I$ , transmitted through  $n$  layers is thus  $(1-a)^nI_0$ . Let us assume the sum of the  $n$  layers to be equal to unit length (1 cm.), then

$$I_1 = (1-a)^nI_0$$

$$\log I_1 = \log I_0 - a,$$

where  $\log (1-a)^n$  has been made equal to  $-a$ .\*

The intensity  $I_2$  of the light which has passed through  $2n$  layers (2 cm.) is according to the formula

$$I_2 = (1-a)^{2n}I_0$$

$$\log I_2 = \log I_0 - 2a,$$

and in general for the intensity of the light transmitted through a layer of  $m$  centimetres we have

$$\log I_m = \log I_0 - ma,$$

whence

$$m = \frac{1}{a}(\log I_0 - \log I_m).$$

Thus, if we know the coefficient of absorption,  $a$ , we can determine the thickness,  $m$ .

This result seems at first sight very useless, as we can measure the thickness much more conveniently otherwise. But we have already said that it is possible to determine the density or concentration in the same way as the thickness. It has been proved by experiment

\*  $1-a$  being always less than unity, the logarithm of  $(1-a)^n$  must always be negative.



that a layer 10 cm. thick of a 1 per cent solution of an absorbent substance produces the same amount of absorption as a 5 cm. layer of a 2 per cent solution, a 2 cm. layer of a 5 per cent solution, etc. If we therefore investigate layers 1 cm. thick, but containing different amounts of substance, the expression  $m = \frac{1}{a}(\log I_0 - \log I_m)$  is proportional

to the concentration, so that the equation affords us the means of calculating the concentration from the intensities of the incident and transmitted light.

The measurement of the intensity is made by means of a photometer, which must enable us to investigate light of one wave-length, as the above considerations apply only to homogeneous light.

Vierordt's apparatus is an ordinary spectroscope of somewhat large calibre, with the slit of the collimator so far altered that the movable edge is divided into two, each half having independent motion from a micrometer screw. The spectrum is thus split up into two contiguous and parallel portions, whose intensities can be independently varied at will. If there is brought before one-half of the slit an absorbent substance, *e.g.* a plate of coloured glass, the absorption spectrum will appear above or below the unchanged spectrum. If we now, by means of two slides in the ocular part of the telescope, obscure the spectrum all but a definite band, we can by widening or narrowing one-half of the slit make the intensities above and below equal. The intensities of the incident and transmitted light are then inversely as the breadth of the slits.

When the half-slit is widened from one side only, as is usual in spectroscopes, the tint of the spectral field is altered, and the comparison of the intensities of the two portions thus rendered difficult. Krüss has sought to do away with this by widening the slit symmetrically on both sides; while Glan and Hüfner prefer to reduce the intensity by a polarising arrangement instead of by altering the slit. Vierordt himself obviated this difficulty by using smoked glass to attain approximate equality, afterwards to be made complete by small adjustments of the breadth of the slit.

The measurement of the rotation of the plane of polarisation was first applied by Gladstone to problems of chemical equilibrium. Quantitative determinations leading to very exact results were made by Jellett on the union of acids with alkaloids. The process rests on the same foundation as the other physical methods. The natural alkaloids are almost all optically active, and to different degrees when in their salts than when free. Let  $\alpha$  and  $\alpha'$  be the rotation for two free alkaloids,  $\beta$  and  $\beta'$  that of their salts with the same acid; we have again the equation

$$\xi = \frac{A - A'}{\alpha + \beta - (\alpha' + \beta')}$$

It need scarcely be mentioned that the angle of rotation refers to

equivalent quantities, *i.e.* to columns of the solutions of such length as to contain quantities of the substances proportional to their formulæ.

In contrast to the heat of neutralisation, and to the changes of volume and of the index of refraction, the direct or indirect application of all which is very general, the photometric method and that based on the rotation of the plane of polarisation are only applicable to a limited number of substances. Still more limited in its use—being practically available for one base only—is the magnetic method, studied almost exclusively by Gustav Wiedemann.

Colloidal ferric oxide, prepared by dialysis of a salt of iron, or by solution of the hydrate in a ferric salt (when of course it is mixed with the latter), is not so strongly magnetic as it is when combined with an acid. If the magnetism of the latter is made equal to 100, then the colloidal oxide has according to the earlier measurements a magnetic power of 22. Later experiments give 16·8 and 15·7, Wiedemann adopting 16·0 as the correct number.

If now for any iron solution the value of the magnetism is found to be *m* for unit weight, that of fully combined oxide being 100, then

$$m = 100(1 - x) + 16 x,$$

where *x* is the quantity of colloidal oxide. Transforming, we have

$$x = \frac{100 - m}{84},$$

so that by determining the magnetism of unit weight we can learn the proportion of ferric oxide free in the solution.

This portion vanishes when a great excess of acid is present. If, on the other hand, the acid and the oxide are in approximately equivalent proportions, then, through the chemical action of the water, a part of the acid is split off, which increases with the amount of water present. Thus in different solutions of ferric chloride containing the quantities of iron in 10 c. cm. denoted by *f*, the following proportions, *x*, of colloidal oxide were found:—

I.		II.	
<i>f</i>	<i>x</i>	<i>f</i>	<i>x</i>
1·606	·014	1·491	·032
1·207	·012	1·119	·043
·806	·025	·747	·056
·404	·032	·375	·083
·202	·036	·184	·097
·138	·092	·129	·117
·071	·112	·062	·141

The solutions of table I. contained ·7 per cent, of table II. 3·1 per cent too little chlorine for the formula  $\text{FeCl}_3$ . Thus in II. the decomposition goes somewhat further.

If alcohol be used as diluent instead of water, no decomposition occurs, even on great dilution, so that we have evidently here to deal with a pronounced action of mass on the part of the water.

Ferric nitrate and sulphate are still more decomposed by water, especially the latter.

With increase of temperature the decomposed portion also increases.

Due account being taken of the influence of temperature on the intensity of the magnetism itself, it was found that in a concentrated solution of the chloride, the action of heat was almost nil, while the nitrate and sulphate showed considerable decomposition.

The ordinary methods of chemical analysis may in all cases be applied to the complete ascertainment of states of equilibrium when these are heterogeneous; for if we set out from a known initial state, the final state is determined if we can estimate the quantity of one of the reacting bodies in it, and this may always be done in heterogeneous systems by mechanical separation of the different portions, which are then separately analysed.

The reader may convince himself that such is actually the case by considering the examples of heterogeneous equilibrium given on pp. 299-303 from this point of view. Whether we are dealing with change of state of aggregation, with solutions, allotropic modifications, the action of acids on insoluble salts, the decomposition of water-vapour by iron, or of barium carbonate by potassium sulphate—the quantities necessary for the complete specification of the state of equilibrium can always be determined either immediately by the ordinary methods of gravimetric or volumetric analysis, or by analytical devices of a more or less simple character. The chemical methods for the determination of the quantities of the substances present on equilibrium need not therefore be specially discussed.

It should be mentioned that chemical methods are applicable even in certain cases of homogeneous equilibrium—when, namely, the possible processes take place so slowly that the analytical operation can be performed in a time in the course of which the state investigated does not sensibly alter. Berthelot and Péan de St. Gilles, for example, availed themselves of this circumstance in their research on esterification, by estimating the free acid remaining after equilibrium had been reached, by titration with baryta solution and litmus. Based on the same assumption, in this case somewhat doubtful, there are experiments by Kreeke (1871) who determined the quantities of colloidal ferric oxide separated under definite conditions from dilute solutions by first precipitating it in the gelatinous form by the addition of a solution of common salt. Ostwald in his researches on the velocity of chemical reactions worked under similar conditions, as will be seen later.

## CHAPTER II

### THE AFFINITY BETWEEN ACIDS AND BASES

AMONG the countless chemical processes, a knowledge of which is of importance for both theory and practice, the phenomenon of neutralisation occupies a prominent position. The general similarity of the process, though performed with the most diverse acids and bases, enables us to institute a comparative study in an uncommonly wide field. The investigation of the actions occurring on the formation and double decomposition of salts marked very early an important scientific advance, for with them Richter discovered the first chemical laws of mass. A similar part has also been reserved to them in respect of the laws of chemical energy.

When an acid acts on a salt, it partially expels the acid of the latter, and unites with the base "in proportion to its quantity and its affinity." If equivalent quantities be taken, the distribution-ratio of the base is a measure of the affinity.

This mode of measuring the affinity was tried by Julius Thomsen as early as 1854, but it was only in 1868 that he began the systematic investigation of a domain at all extensive. The particulars of such experiments have already been given (p. 327), so that it will now be sufficient after a few supplementary remarks to state the results obtained.

In the experiments one acid was allowed to act on an equivalent quantity of the sodium salt of another acid. We have then in the general equation for equilibrium of p. 298,  $p = q = 1$  and  $p' = q' = 0$ , so that

$$c(1 - \xi)^2 = c'\xi^2$$

$$\frac{(1 - \xi)^2}{\xi^2} = \frac{c'}{c} \text{ and } \frac{1 - \xi}{\xi} = \sqrt{\frac{c'}{c}}.$$

Now  $1 - \xi$  is the portion of the neutral salt which has remained undecomposed, and therefore also the part of the base retained by the original acid, while  $\xi$  is the decomposed portion of the salt, and also the part of the base united to the new acid. The ratio  $\frac{1 - \xi}{\xi}$  is

consequently a measure of the relative chemical affinity of the two acids. Thomsen, who imagined that the thermal effect measured the affinity, introduced instead of this the new designation avidity. This is so far unnecessary as there is no apparent relation between the thermal effect and the ratio of distribution. Sulphuric acid, for example, which has a much greater heat of neutralisation than nitric acid, is expelled from its sodium salt by the latter to the extent of two-thirds, so that, contrary to the traditional opinion, nitric acid, and also hydrochloric acid, must be regarded as "stronger" than sulphuric acid.

The proper measure of the chemical activity of the acids is really the specific velocity of reaction  $c$ . From the experiments just described we cannot directly obtain this, but only the ratio it bears to other similar coefficients. According to the formula, the ratio  $\left(\frac{1-\xi}{\xi}\right)^2$  is

equal to  $\frac{c'}{c}$ , the ratio of the coefficients of velocity, *i.e.* the ratio of the coefficients of velocity is equal to the square of the ratio of the avidities.

The following table contains a collection of the avidities or relative affinities calculated by Thomsen from his own experiments. The numbers are all referred to hydrochloric acid as unit, and are for one equivalent of each of the various acids acting against one equivalent of soda. They are only approximate values, as Thomsen himself is careful to emphasise.

Acid.	Avidity.	Heat of Neutralisation.
Hydrochloric . . . . .	1.00	137 K
Nitric . . . . .	1.00	137 „
Hydrobromic . . . . .	.89	138 „
Hydriodic . . . . .	.70	137 „
Sulphuric . . . . .	.49	157 „
Selenic . . . . .	.45	152 „
Trichloroacetic . . . . .	.36	139 „
Orthophosphoric* . . . . .	.25	148 „
Oxalic . . . . .	.24	141 „
Monochloroacetic . . . . .	.09	143 „
Hydrofluoric . . . . .	.05	163 „
Tartaric . . . . .	.05	127 „
Citric . . . . .	.05	130 „
Acetic . . . . .	.03	134 „
Boric ( $\text{H}_3\text{BO}_3$ ) . . . . .	.01	100 „
Silicic . . . . .	.00	52 „
Hydrocyanic . . . . .	.00	28 „

The numbers have the following meaning. If, for example, one equivalent of sulphuric acid acts on one equivalent of sodium monochloracetate, then the soda distributes itself between the two acids in

\* For one molecule  $\text{H}_3\text{PO}_4$ .

the ratio  $\cdot 49 : \cdot 09$ . From  $\frac{1 - \xi}{\xi} = \frac{\cdot 49}{\cdot 09}$

it follows that  $\xi = \cdot 155$ , *i.e.* the monochloroacetic acid retains 15·5 per cent of the soda, while the sulphuric acid secures the remaining 84·5 per cent.

The heats of neutralisation have been noted alongside. A very slight consideration serves to show that they have nothing at all to do with the avidities. The greatest heats of neutralisation are possessed by hydrofluoric, sulphuric, selenic, orthophosphoric, and the like acids, all of which are weaker, many of them much weaker, than hydrochloric and nitric acids.

Daily experience in the laboratory teaches us that the affinity of acids for bases is of such a nature as to appear a specific property of the acids. When we say that carbonic acid is a weak acid and sulphuric acid a strong one, we do not thereby mean that this is so with respect to this or the other base, but that it is so in general. Here there lies the fundamental assumption that the reciprocal affinity between an acid and a base depends on something peculiar to the acid and something else peculiar to the base. Acetic acid, for instance, is more feebly united to all bases than sulphuric acid, no matter whether we compare the salts of the powerful base potash or of the weak base alumina.

Thomsen was the first to propound the question, whether the base had any influence on the relative affinity or not; and gave his decision that it had. In his experiments he employed sulphuric and hydrochloric acids, on which he acted with the following bases:—potash, ammonia, magnesia; manganous, ferrous, zinc, cobalt, nickel, and cupric oxides. As most of these bases are insoluble in water, he did not determine their heat of neutralisation directly, but applied the theorem (p. 328) that the difference of the heats of neutralisation of two acids is equal to the difference of the heats of reaction between each acid and the neutral salt of the other.

The experiments performed by Thomsen consisted therefore of measurements of the heat of reaction of hydrochloric acid on the sulphates ( $Q_1$ ), and of sulphuric acid on the chlorides ( $Q_2$ ). For all bases there was a secondary reaction between the sulphate and the free sulphuric acid, just as we saw to be the case with soda. Thomsen did not make a similar extensive series of measurements on the action of the sulphuric acid on each sulphate, but determined the heat of reaction for equivalent quantities, and assumed the heat of reaction (as a function of the quantity of sulphuric acid) to be proportional to the heat measured in the case of sodium sulphate. The calculation is made according to the formula on p. 328.

His results are contained in the following table. In the first column we have the symbols of the metals, next comes the decom-

posed quantity  $\xi$  of the sulphate, and then the relative affinity (or avidity)  $\frac{1-\xi}{\xi}$ . The last column contains the thermal effect  $q_1$  of the reaction between equivalent quantities of the sulphates and sulphuric acid, a magnitude which we shall require later.

	$\xi$	$\frac{1-\xi}{\xi}$	$q_1$
Na <sub>2</sub>	·666	·50	- 18·7 K
K <sub>2</sub>	·636	·57	- 16·5 „
Am <sub>2</sub>	·640	·56	- 14·1 „
Mg	·590	·69	- 10·8 „
Mn	·586	·70	- 9·0 „
Fe	·573	·74	- 9·0 „
Zn	·577	·73	- 8·8 „
Co	·566	·76	- 8·3 „
Ni	·563	·78	- 7·9 „
Cu	·553	·81	- 6·8 „

We see that the decomposed quantity  $\xi$  of sulphate is not the same for the different salts, but decreases pretty regularly, so that the relative affinity of sulphuric acid with respect to hydrochloric acid is not constant, but depends upon the base; it is largest for copper and smallest for sodium. Thomsen is of opinion that it may be considered constant for the alkalis, on the one hand, and for the bases of the magnesia group, on the other; however, the difference between Mg and Cu is ·12, as great as the difference between K<sub>2</sub> and Mg, so that it is better to assume that the values vary continuously.

Thomsen had confined his experiments to hydrochloric and sulphuric acids. Now as the behaviour of the latter is more complicated than was at first supposed, the results could give no final decision as to whether the nature of the base had any influence on the affinity of acids for them or not.

For this reason Ostwald (1877) repeated the measurements volumetrically and extended them by adding a series for nitric acid. His results were as follows:—

#### RELATIVE AFFINITIES OF ACIDS.

	$\frac{\text{Nitric}}{\text{Sulphuric}}$	$\frac{\text{Hydrochloric}}{\text{Sulphuric}}$	$\frac{\text{Hydrochloric}}{\text{Nitric}}$
Potash	$\frac{·667}{·333} = 2·00$	$\frac{·659}{·341} = 1·94$	$\frac{1·94}{2·00} = ·97$
Soda	$\frac{·667}{·333} = 2·00$	$\frac{·657}{·343} = 1·92$	$\frac{1·92}{2·00} = ·96$
Ammonia	$\frac{·652}{·348} = 1·88$	$\frac{·644}{·356} = 1·81$	$\frac{1·81}{1·88} = ·96$
Magnesia	$\frac{·638}{·362} = 1·76$	$\frac{·635}{·365} = 1·74$	$\frac{1·74}{1·76} = ·99$
Zinc oxide	$\frac{·617}{·383} = 1·61$	$\frac{·605}{·395} = 1·53$	$\frac{1·53}{1·61} = ·95$
Cupric oxide	$\frac{·591}{·409} = 1·44$	$\frac{·584}{·416} = 1·40$	$\frac{1·40}{1·44} = ·97$

The numbers in the table give the ratio in which one equivalent of the base is distributed between equivalents of the two acids. The two first columns are deduced directly from experiment, the third is the quotient of the second by the first, for the critical case in which the method gives no result occurs with hydrochloric and nitric acids.

Corresponding to Thomsen's experiments the two first columns are variable. On the other hand, the relative affinity of hydrochloric and nitric acids is independent of the base and remains constant.

In the case of the experiments with sulphuric acid there is, besides the action of the acid on the base, a secondary action on the neutral sulphate (p. 340), which to a certain extent obscures the former. If we compare the numbers representing the secondary action for the various salts, we see the same order as in the foregoing table, the action being greatest with potash, least with cupric oxide. Consequently the action on the base is the more interfered with, the greater the action is on the neutral salt, and thus, although it is not proved, it is at least rendered probable, that the affinity of sulphuric acid also for the base is independent of the nature of the latter.

From this result important conclusions may be drawn, but before we proceed to these we shall look at some further measurements which place the first securely on a broader basis.

Ostwald in 1878 investigated a large number of acids with respect to their relative affinity for potash, soda, and ammonia. To this end he used the volumetric method, and also took advantage of the help offered by the indices of refraction. For details of the experiments the original papers must be consulted; merely the final results are given here in tabular form.

RATIOS OF DISTRIBUTION.

Acids.	Potash.	Soda.	Ammonia.	Mean.
Nitric: dichloracetic . . . .	77	77	75	76
Hydrochloric: dichloracetic . .	74	75	73	74
Trichloracetic: dichloracetic . .	{ 70 73	{ 71 71	{ 70 72	71
Lactic: dichloracetic . . . .	8	9	11	9
Trichloracetic: monochloracetic .	92	92	92	92
Trichloracetic: formic . . . .	97	96	97	97
Lactic: formic . . . . .	43	46	48	46
Acetic: formic . . . . .	25	23	23	24
Butyric: formic . . . . .	21	21	19	20
Isobutyric: formic . . . . .	19	19	18	19
Acetic: butyric . . . . .	54	52	53	53
Acetic: isobutyric . . . . .	56	51	53	53
Formic: propionic . . . . .	78	80	79	79
Formic: glycollic . . . . .	43	44	45	44

One equivalent of the first-named acid acted on one equivalent of the neutral salt of the second: the numbers give the amount per cent of the base abstracted by the first acid from the salt.

If we compare the ratios obtained for potash, soda, and ammonia, we



always find them agreeing within the error of observation. The deviations are quite irregularly distributed, and the conclusion drawn for hydrochloric and nitric acids—that the relative affinity is independent of the nature of the base—is confirmed for all the monobasic acids here investigated. The observed numbers have therefore been employed to give a mean value in each case.

A further confirmation of the principle and of the above numbers was afforded by the optical investigations. In this case, however, the determination of the ratios is much less certain owing to the greater experimental error.

We can now use the principle, without any further hypothetical assumption, for the deduction of a second principle of equal scope. If we write the absolute affinity of an acid A for a base B as  $f(A, B)$ , a function of both, then the principle is expressed by the equation

$$\frac{f(A, B)}{f(A', B)} = \frac{f(A, B')}{f(A', B')}$$

where A and A' are two acids, B and B' two bases. Exchanging the means we have

$$\frac{f(A, B)}{f(A, B')} = \frac{f(A', B)}{f(A', B')}$$

This signifies that the relative affinity of the bases is independent of the nature of the acid. Although not yet put to the test of experiment, this principle is as certain as the first one.

The above relations are only possible on condition that each function  $f(A, B)$  can be resolved into two factors  $\rho(A)$  and  $\phi(B)$ , of which one depends on A alone, the other on B alone—

$$f(A, B) = \rho(A) \cdot \phi(B).$$

The affinity between an acid and a base is the product of two specific coefficients of affinity, one belonging to the acid, the other to the base.

In this way we arrive at a general representation of the affinities which come into play on neutralisation. If we have determined the relative affinities of the various acids for one base, and of the various bases for one acid, a base B and an acid A being arbitrarily chosen as standards, then the values of the affinities may be tabulated as follows:—

	$\rho(A)$	$\rho(A')$	$\rho(A'')$	$\rho(A''')$
$\phi(B)$	.	.	.	.
$\phi(B')$	.	.	.	.
$\phi(B'')$	.	.	.	.
$\phi(B''')$	.	.	.	.

In this table, the affinity of any base for any acid is obtained by multiplying the first terms of the row and column corresponding. A point of difference from the tables of similar appearance that we have

often employed lies in the ratios of the rows or columns being here constant, and not their differences.

The calculation of the numbers given above leads to the following values of  $\frac{\xi}{1-\xi}$ , with respect to nitric acid as unity :—

Acid.	Ostwald.	Thomsen.
Nitric . . . . .	1·00	1·00
Hydrochloric . . . . .	·98	1·00
Trichloracetic . . . . .	·80	·36
Dichloracetic . . . . .	·33	—
Monochloracetic . . . . .	·070	·09
Glycollic . . . . .	·050	—
Formic . . . . .	·039	—
Lactic . . . . .	·033	—
Acetic . . . . .	·0123	·03
Propionic . . . . .	·0104	—
Butyric . . . . .	·0098	—
Isobutyric . . . . .	·0092	—
Tartaric . . . . .	·052	·05
Malic . . . . .	·00282	—
Succinic . . . . .	·00145	—

Thomsen's avidities have been added in a separate column. The two series agree as far as order of magnitude is concerned; with regard to the numerical differences, the much greater uncertainty of the thermochemical experiments must be taken into consideration. Thomsen's value for trichloracetic acid has doubtless been displaced so far through some slip; we shall see below a number of other experiments on its affinity, all of which confirm the number ·80. It should be remarked, however, that these values for the relative affinity are by no means to be considered final. Although the order of succession is not likely to experience any change, still the numbers are affected by many collateral circumstances, which all go to render the numerical values somewhat uncertain.

Many salts insoluble in water are dissolved by dilute acids when these can form soluble salts with the bases. It scarcely needs mention that this apparent solution has its origin in a decomposition; calcium oxalate dissolves in hydrochloric acid because the latter converts it into oxalic acid and calcium chloride, both of which are soluble in water. The phenomena here observed are in many ways analogous to those of pure solution, say of a salt in water, and specially in so far as there is for every acid a state of saturation uninfluenced by an excess of the solid substance. The solubility increases with increase of temperature. On the other hand, the chemical character of the process is shown in the circumstance that addition to the solvent of one of the products of decomposition (calcium chloride or oxalic acid in the above example) diminishes the solubility (cf. p. 302).

This process may be successfully employed to determine the

coefficients of affinity of the acids in virtue of the following considerations.

If an acid of active mass  $p$  acts on an insoluble salt, a portion  $\xi$  of the latter will be decomposed. The active mass of the acid will therefore be diminished to  $p - \xi$ , and the two products of the decomposition will each have the active mass  $\xi$ ;  $h$  may be put as the constant active mass of the solid. The equation for equilibrium is therefore (p. 302)

$$c(p - \xi)h = c'\xi^2,$$

whence 
$$\frac{c}{c'} = \frac{\xi^2}{(p - \xi)h} \text{ and } \sqrt{\frac{c}{c'}} = \frac{\xi}{\sqrt{(p - \xi)h}}.$$

The coefficients of velocity  $c$  and  $c'$  measure the action of the acids on the base,  $c$  corresponding to the free acid,  $c'$  to the acid in the insoluble salt. Now it has been already shown that the "avidity" of two acids for the same base is equal to the square root of the ratio of the corresponding velocities of reaction. As the nature of the base has no influence on the relative affinities (p. 341), the above expression

$$\sqrt{\frac{c}{c'}} = \frac{\xi}{\sqrt{(p - \xi)h}} \text{ gives the relative affinity of the two acids at once.}$$

In this equation the coefficient  $h$  of the action of the solid is still unknown. If we make a similar experiment, however, with another acid, we obtain a new equation

$$\sqrt{\frac{c_1}{c'}} = \frac{\xi_1}{\sqrt{h(p_1 - \xi_1)}},$$

which, being divided into the first one, gives us

$$\sqrt{\frac{c}{c_1}} = \frac{\xi}{\xi_1} \sqrt{\frac{p_1 - \xi_1}{p - \xi}}.$$

On the right-hand side everything is now known, and so we find from the expression the relative affinity of the two solvent acids. By repeating the experiment with other acids we obtain their relative affinity similarly in terms of an arbitrary unit.

The first experiments according to this method were made with zinc sulphide. The acids to be investigated were brought into contact with a sufficient quantity of hydrated zinc sulphide at the ordinary temperature, the mixture being shaken for twenty-four hours by means of a small machine for the purpose. The quantity of zinc sulphide which had passed into solution was determined by estimating the sulphuretted hydrogen liberated, by means of a very weak standard solution of iodine.

The following tables give the dissolved quantities of zinc sulphide in terms of the total quantities which would have been in solution had the decomposition been complete. The acids were at different stages of dilution, the number of litres containing one gram-molecule being given in the first

column—thus 4 l. for hydrochloric acid denotes a solution in which 36·46 g. of hydrogen chloride are contained in 4 litres of water.

## HYDROCHLORIC ACID.

Dilution.	$\xi$	$\frac{\xi}{\sqrt{1-\xi}}$
1 l.	·0411	·0120
2 l.	·0190	·0387
4 l.	·00863	·0351
8 l.	·00396	·0322

## SULPHURIC ACID.

Dilution.	$\xi$	$\frac{\xi}{\sqrt{1-\xi}}$
2 l.	·0238	·0241
4 l.	·01185	·0210
8 l.	·00600	·0243
16 l.	·00301	·0244

For the normal solution,  $p$  has been made equal to 1; for the others it is consequently  $\frac{1}{2}$ ,  $\frac{1}{4}$ , and  $\frac{1}{8}$ .

Taking the quotients of the corresponding members of the last columns in the two tables, we see that the relative affinity, sulphuric acid : hydrochloric acid, is ·574, ·621, ·693, and ·758; it therefore varies with the dilution. The volumetric experiments were for a dilution of about 3 l., and give for the relative affinity with respect to zinc ·65, the mean of the values for 2 l. and 4 l. being here ·657—almost the same as it happens. The fact that the relative affinity of the sulphuric acid increases with the dilution has the same probable cause as its variation with the nature of the base—namely the formation of acid salts (p. 340), which has progressively decomposed with increasing quantities of water.

That this is so can be shown (and approximate measurements made) by the method before us. Equivalent quantities of neutral sulphates and free sulphuric acid were brought together in aqueous solution and treated with zinc sulphide.

The following table gives the values of  $\frac{\xi}{\sqrt{1-\xi}}$  obtained in this way:—

Dilution.	$\text{H}_2\text{SO}_4$	+ $\text{K}_2\text{SO}_4$	+ $\text{Na}_2\text{SO}_4$	+ $(\text{NH}_4)_2\text{SO}_4$	+ $\text{MgSO}_4$
2 l.	·0241	·0156	·0168	·0171	·0196
4 l.	·0240	·0174	·0186	·0187	·0207
8 l.	·0243	·0187	·0197	·0208	·0218
16 l.	·0244	·0191	·0198	·0219	·0225

We see from these numbers that the action of the free sulphuric acid is weakened by the addition of sulphates, more by potassium than by magnesium sulphate, and more at less than at greater dilutions. The order of succession is quite the same as in the volumetric experiments (p. 340).

Finally, it may be mentioned that when two acids act together on zinc sulphide the quantity of hydrogen sulphide formed is the sum of the quantities which would be liberated by the acids separately. With a mixture of sulphuric and hydrochloric acids the numbers obtained were as follows:—

Dilution.	$\xi$ Observed.	$\xi$ Calculated.
1 l.	·0327	·0330
2 l.	·0309	·0309
4 l.	·0297	·0293
8 l.	·0282	·0279

A much more suitable material than zinc sulphide, which is difficult to procure of uniform quality, is to be found in calcium oxalate, which, when in the form of the easily obtainable hydrate,  $\text{CaC}_2\text{O}_4 + \text{H}_2\text{O}$ , gives very constant values. It has, besides, the valuable property that equilibrium can be reached with it in a very short time; the mixture of oxalate and acid has only to be shaken a few moments to bring into solution as much as can possibly be dissolved under the given circumstances.

The quantity of the salt dissolved is most easily determined by titration with potassium permanganate. If the acid used is indifferent towards this reagent, the solutions may be titrated directly, otherwise the oxalate is first precipitated by addition of ammonia and a little calcium chloride or ammonium oxalate.

The following table contains the values  $\frac{\xi}{\sqrt{1-\xi}}$ , the active mass of the acid having been always made equal to unity:—

RELATIVE AFFINITIES.					
Acid.	Normal.	Decinormal.	(Volumetric).		
Nitric . . . .	1·00	1·00	1·00		
Hydrochloric . . . .	·90	·979	·98		
Hydrobromic . . . .	·851	·990	—		
Chloric . . . .	·932	·998	—		
Formic . . . .	·0233	·1290	·039		
Acetic . . . .	·0094	·0735	·0123		
Monochloracetic . . . .	·046	·213	·070		
Dichloracetic . . . .	·165	·488	·33		
Trichloracetic . . . .	·578	·899	·80		
Lactic . . . .	·037	·133	·033		
Succinic . . . .	·0185	·0930	·0145		
Malic . . . .	·0455	·1205	·0282		
Tartaric . . . .	·0578	·1416	·052		
Citric . . . .	·0275	·1441	—		

For comparison, the numbers obtained by the volumetric method have been added. They fall for the most part between the numbers for the normal and for the decinormal solutions with calcium oxalate, which might be expected, as they were found for  $\frac{1}{3}$  normal solutions. The order of magnitude is the same, and even the numerical agreement is as good as could be desired, considering the difficulty of the volumetric measurements and the different character of the methods employed.

The very considerable influence of dilution on the relative affinity of weak acids is remarkable; the affinities increase four or even five-

fold on passage from normal to decinormal solutions. The regularities here observed will be discussed in greater detail in the sequel.

Other insoluble salts behave like calcium oxalate. Zinc oxalate and barium chromate have been investigated, and yield results similar to the above. Recently, too, experiments have been conducted with potassium hydrogen tartrate and with the sulphates of barium, strontium, and calcium; all these have given much the same values. Isolated small deviations still remain to be explained. They are not sufficiently important to render the results doubtful, but, on the other hand, they are of importance as leading us to the recognition of secondary actions, which are present under all circumstances, but have not been considered in the general construction of the theory.

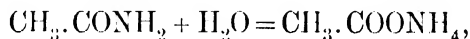
## CHAPTER III

### SPECIFIC COEFFICIENTS OF AFFINITY

THE property possessed by acids of acting in proportion to a definite coefficient is not confined to salt-formation. There are numerous other reactions conditioned by acids as such, and in all of these the same coefficients of activity belonging to the acids regulate the action.

The first case to be investigated in this respect has still some slight connection with the affinities appearing in the phenomenon of neutralisation. An aqueous solution of acetamide is converted by the influence of acids into ammonium acetate, the elements of water being taken up; and the acetate being further changed by the acid, if it is strong, into the corresponding ammonium salt and free acetic acid.

The primary process thus takes place between acetamide and water—



the acid having a “predisposing” action, as the conversion by water alone takes place with extreme slowness. The explanation of such “predisposing” affinities offers no difficulty from the point of view of the molecular theory. In the case in question we have to imagine that the molecules of acetamide in the aqueous solution are more or less loosened by their continuous movements. At a definite degree of loosening, the chemical affinity of the components of the acetamide ( $\text{CH}_3\text{CO}$  and  $\text{NH}_2$ ) for the components of water ( $\text{OH}$  and  $\text{H}$ ) is great enough to allow the transformation to take place. If at the same time a substance is present which has a strong affinity for one of the products of decomposition, attracting it therefore with considerable force, a less degree of internal loosening in the acetamide molecules will suffice to enable the more powerful separative forces to prevail, than when water alone is acting. The acceleration of the action will also be the more considerable, the greater the affinity between ammonia and the acid, *i.e.* the stronger the latter proves in the sense already indicated.

The investigation of the differences in the action of the various acids does not now conduct as in the former cases to different con-

ditions of equilibrium, but to different velocities of reaction. The relation between the two has already been stated:—in a reaction of the second order the coefficients of distribution are as the square roots of the coefficients of velocity. This proposition was, it is true, deduced in the first instance for one and the same process, but it may be extended as above by reason of the empirically discovered property of the coefficients of distribution of acids with respect to bases, that they are the products of two coefficients, one depending only on the base, the other only on the acid (p. 342).

The coefficient of distribution for the action of two acids  $A_1$  and  $A_2$  on the same base  $B$  is of the form  $k = \frac{\phi(A_1)\psi(B)}{\phi(A_2)\psi(B)} = \frac{\phi(A_1)}{\phi(A_2)}$ . Now this is equal to the square root of the ratio of the two velocities of reaction, so

$$\frac{c_1}{c_2} = \frac{\phi^2(A_1)}{\phi^2(A_2)}.$$

The coefficients of velocity for the action of acids on any base are thus proportional to the squares of the coefficients of distribution or relative affinities. As has been mentioned, the proposition can be empirically extended so as to include the coefficients of velocity of all reactions brought about by acids as such. By measurement of any process of this sort we shall therefore, in like manner, arrive at a determination of the strength of acids.

The transformation of acetamide occurs in dilute solution even at the ordinary temperature when acids are present, but so slowly that long periods are requisite for an exact study of the process. At  $65^\circ$  the reaction proceeds at a convenient rate, so at that temperature most of the experiments have been conducted.

Since the decomposition of acetamide by acids is a reaction of the second order, corresponding, *e.g.*, to the equation



equivalent quantities of acetamide and acid disappearing,\* the velocity-equation that applies is the one developed on p. 295, viz.

$$\frac{x}{A-x} = Ac\theta,$$

where  $\theta$  is the time, equivalent quantities of the two components being always taken. In individual cases there is a fair agreement between the theoretical course of the reaction and actual experiment, but this agreement is by no means general, as the process is not free from secondary reactions. In particular, the neutral salt which is gradually formed, acts in a characteristic manner by intensifying the action of acids of the type of hydrochloric or nitric acid in proportion to its quantity. It appears from

\* The acetic acid simultaneously produced is almost without influence on the process.



researches to be spoken of later, that weak acids, on the other hand, are still further weakened by their neutral salts, the influence being greater the weaker the acids are. Consequently in experiments with strong acids the coefficient of velocity will not remain constant during the reaction, but increase with the time expired from the commencement; with weak acids it will decrease; and only with acids of moderate strength (trichloroacetic acid) will the action of the salt be so small that the process of transformation will take place according to the simple assumption of a constant coefficient of velocity.

In the first place, in order to institute a comparison of the different values free from arbitrary selection, the time is calculated in which the reaction has run exactly half its course. For this we have

$$\frac{\frac{1}{2}A}{A - \frac{1}{2}A} = A c \theta \text{ or } c = \frac{1}{A \theta}.$$

On account of the secondary reactions alluded to above, the reciprocals of the times taken for half-completion of the transformation do not give the true velocities of reaction. These can only be ascertained by the employment of correspondingly complicated equations, and the determination of the new coefficients appearing in them. Since, however, the relative affinities obtained from the distribution of a base between two acids and from the decomposition of insoluble salts are influenced in the same way by quite similar collateral circumstances, one ought to expect, if not identity, at least some analogy between the corresponding series of numerical values.

The following table contains in columns I and II the relative velocities of reaction, *i.e.* the reciprocals of the times taken for half-completion of the reaction at 65° and 100°, the value for hydrochloric acid being taken as unity. Columns III and IV contain the square roots of these numbers, which ought to be equal to the relative affinities of the preceding tables (pp. 343, 346); of these, there have been indicated the values obtained by the volumetric method (V), and by the solution of calcium oxalate (VI).

Acid.	I	II	III	IV	V	VI
Hydrochloric .	1·000	1·000	1·00	1·00	0·98	·90
Nitric .	·959	·933	·98	·97	1·00	1·00
Hydrobromic .	·974	·969	·98	·98	·95	·85
Trichloroacetic .	·639	—	·80	—	·80	·58
Dichloroacetic .	·1663	—	·408	—	·33	·165
Monochloroacetic	·01687	—	·130	—	·070	·046
Formic .	·00266	·00233	·0516	·0483	·039	·0233
Lactic .	·00263	·00234	·0513	·0485	·033	·037
Acetic .	·00055	—	·0234	—	·0123	·0094
Sulphuric .	·428	·353	·654	·594	·667	·616
Oxalic .	·0509	·0420	·226	·205	—	—
Tartaric .	·00564	·00536	·0751	·0732	·052	·058
Malic .	·09218	—	·0467	—	·0282	·046
Succinic .	·00065	·000624	·0255	·0205	·0145	·0185
Citric .	·00161	·00161	·0401	·0401	—	·0275
Phosphoric .	—	·00128	—	·0358	—	—
Arsenic .	—	·00124	—	·0353	—	—

The order of magnitude of these numbers obtained in ways so dissimilar, is in every case the same; especially do the measurements of velocity with acetamide approximate closely to the values yielded by the equilibrium experiments. The agreement is the more remarkable that the experiments were conducted at widely differing temperatures and concentrations.

The various measurements serve therefore to prove that acids in reality are active in proportion to definite coefficients, which are quite independent of the particular character of the chemical process. They are further an experimental confirmation of the connection required by theory between conditions of equilibrium and velocities of reaction, and as such are of more general import.

In the first few instants of a chemical process the secondary reactions have the smallest influence, for then the substances to which they are due are present in very small quantity, if present at all. We shall therefore, by applying the theoretical formula to the first observation of each series, obtain values of  $Ac$  diverging from the true coefficients of velocity in the same sense but to a much smaller degree than the velocities observed for the half-completed reaction.

In the following table the values of  $Ac$  have been multiplied by 1,000,000 to avoid an unnecessary number of ciphers; the last column contains the values of the coefficients of velocity referred to hydrochloric acid as unity:—

Acid.	Temp.	$\theta$	$x$	$A - x$	$Ac$ .	Coeff.
Hydrochloric . . .	66°	15	442	2238	1317	1·00
„ . . .	100°	2	665	1995	16670	1·00
Nitric . . .	65°	15	425	2255	1258	·955
„ . . .	100°	2	651	2009	16200	·972
Hydrobromic . . .	65°	15	433	2247	1286	·976
„ . . .	100°	2	659	2001	16490	·989
Trichloracetic . . .	65°	15	313	2367	881	·670
Dichloracetic . . .	65°	30	237	2441	323	·245
Monochloracetic . . .	65°	480	420	2255	38·8	·0295
Formic . . .	65°	2880	446	2214	7·00	·00532
„ . . .	100°	120	278	2382	96·8	·00581
Lactic . . .	65°	2880	407	2253	6·25	·00476
„ . . .	100°	240	416	2244	77·2	·00464
Acetic . . .	65°	14400	330	2330	·984	·000747
Sulphuric . . .	65°	15	261	2414	720	·547
„ . . .	100°	3	555	2105	8780	·527
Oxalic . . .	65°	60	315	2359	222·5	·169
„ . . .	100°	15	665	1995	2225	·134
Tartaric . . .	65°	1440	469	2166	15·90	·0121
„ . . .	100°	120	549	2111	217	·0130
Malic . . .	65°	1440	314	2348	9·28	·00704
Succinic . . .	65°	2880	183	2477	2·57	·00195
„ . . .	100°	480	304	2356	2·72	·00163
Citric . . .	65°	1440	349	2311	10·50	·00797
„ . . .	100°	240	527	2131	103·3	·00620
Phosphoric . . .	100°	15	268	2392	747	·0449

It must be repeated that these numbers for the relative coefficients of velocity are only approximative. They have been calculated simply for the purpose of comparing them with more trustworthy numbers obtained from methods less subject to secondary influences. It is, besides, instructive to see how largely the secondary actions influence the primary ones—the coefficients of weak acids for the half-completed reaction sink as low as half the values, themselves too small, contained in the above table.

The experiments with acetamide have proved especially suited for the comparison of coefficients of equilibrium with those of velocity, inasmuch as they are affected by secondary circumstances in the same sense as the equilibrium experiments, so that the effect of these in the comparison is to some extent eliminated. However, the true values of the coefficients of velocity can only be approximately obtained by this method; the values found for strong acids are too great, for weak acids too small.

A method proposed by Ostwald (1883) is more exempt from such errors. When aqueous solutions of ethyl acetate, methyl acetate, and similar compounds are allowed to stand at the ordinary temperature, the ester undergoes a very slow decomposition into alcohol and acid, perhaps 1 per cent of the whole being decomposed in two or three days. If a little dilute hydrochloric or any other strong acid be added, it is found that all the ester is hydrolysed within four and twenty hours. The course of the reaction can be easily followed by titration with dilute baryta solution, the acidity of the liquid increasing proportionally to the quantity of ester decomposed.

The foreign acid experiences no alteration; we have therefore here to deal with a well-characterised contact-action, in which a substance seems to act merely by its presence, without itself taking part in the material reaction. It was proved by a special experiment that in the action of hydrochloric acid on methyl acetate there was not present at any time an observable quantity of methyl chloride, for titration with a solution of silver always gave the full quantity of chlorine, whereas if methyl chloride had been formed, the chlorine it contained would not have been attacked and precipitated by the silver nitrate.

Since, during the process, the quantity of the ester alone suffers alteration, we have to do with a reaction of the first order, which progresses according to the equation

$$\lg \frac{B}{B-x} = Ac\theta,$$

B being the quantity of ester, A the quantity of acid. In contrast to the formula developed on p. 293, the factor A in addition enters the right-hand side of the equation, because the quantity of the ester as well as of the acid is of influence on the reaction. The following example for hydriodic acid shows how close is the agreement between theory and experiment—

$\theta$	$x$	$\log \frac{B}{B-x}$	$Ac$
33	223	·0733	·00234
63	389	·1457	·00231
93	533	·2147	·00231
123	658	·2857	·00232
160	786	·3716	·00232
200	902	·4685	·00234
300	973	·5406	·00235
240	1102	·7122	·00237
360	1173	·8477	·00235
428	1232	1·0088	·00240
480	1265	1·1294	·00234
$\infty$	1367		

Mean ·002341

The first column gives the time in minutes ;  $x$  is the amount of ester decomposed, measured in arbitrary units. In the third column are the values of  $\log \frac{B}{B-x}$ ; in the fourth the same numbers divided by the time ; which quotient according to the theory should be constant, and proves, indeed, to be so.

For different quantities of ester with a constant quantity of acid, the coefficient of velocity  $c$  ought to be as a first approximation independent of this alteration. The formula may be written

$$\log \frac{B}{B-x} = \log \frac{1}{1 - \frac{x}{B}} = Ac\theta ;$$

and thus  $x$  and  $B$  must remain proportional. Small deviations may appear, for the medium in which the process takes place varies somewhat with varying quantities of ester, and consequently the coefficient of velocity undergoes slight changes.

The experiments to test this were so conducted that 10 c. cm. of normal hydrochloric acid were added to 2, 1, ·5, and ·3 c. cm. of methyl acetate, and the whole diluted to 15 c. cm. The measurements yielded results as follows :—

Methyl acetate.	$B$	$Ac$
2 c. cm.	2596	·002419
1 „	1434	·002196
·5 „	766	·002071
·3 „	466	·001999

Thus the coefficient  $c$  does not remain constant, but decreases with diminishing quantity of ester. The experiments, however, were not quite properly arranged, the quantity of water being variable. It would have been better to add the methyl acetate always to the same quantity of acid, for the active quantity of the acid can obviously only be considered with respect to that portion of the total volume not occupied by the ester, while the total

volumes were made equal in the above test. If we correct the values by multiplying by  $\frac{13}{15}$ ,  $\frac{14}{15}$ ,  $\frac{14.5}{15}$ , and  $\frac{14.7}{15}$ , we get the following numbers:—

Ac = .002097, .002051, .001996, and .001996 respectively. The variation here is much smaller; it only amounts to about 5 per cent for an alteration of the quantity of methyl acetate in the proportion of 7 : 1. We may thus look upon the proportionality between x and B and the independence of the coefficient of velocity on the amount of ester as holding true within tolerably wide limits.

Numerous acids were investigated according to the method just described, 10 c. cm. of normal acid and 1 c. cm. of methyl acetate being always diluted to 15 c. cm. The temperature was 26°. The table gives in the first column the values of Ac multiplied by 10,000, and in the second the relative coefficients with respect to hydrochloric acid as unity.

Acid.	I	II	III
Hydrochloric . . . .	24.12	1.00	1.00
Hydrobromic . . . .	23.70	.983	.976
Hydriodic . . . . .	23.33	.963	—
Nitric . . . . .	22.06	.915	.955
Chloric . . . . .	22.78	.944	—
Sulphuric . . . . .	13.19	.547	.547
Methylsulphuric . . .	24.30	1.007	—
Ethylsulphuric . . . .	23.80	.987	—
Propylsulphuric . . . .	23.63	.980	—
Isobutylsulphuric . . .	23.41	.971	—
Amylsulphuric . . . .	23.08	.959	—
Ethanesulphonic . . . .	23.61	.979	—
Isethionic . . . . .	23.57	.978	—
Benzenesulphonic . . .	23.94	.991	—
Formic . . . . .	.316	.01310	.0053
Acetic . . . . .	.0833	.00345	.00075
Propionic . . . . .	.0733	.00304	—
Butyric . . . . .	.0721	.00299	—
Isobutyric . . . . .	.0646	.00264	—
Monochloroacetic . . . .	1.036	.0430	.0295
Dichloroacetic . . . . .	5.56	.2304	.245
Trichloroacetic . . . .	16.45	.6820	.670
Lactic . . . . .	.2172	.00901	.0048
Oxyisobutyric . . . . .	.3031	.00921	—
Trichlorolactic . . . .	1.665	.0690	—
Pyruvic . . . . .	1.616	.0670	—
Oxalic . . . . .	4.21	.1746	.169
Malonic . . . . .	.692	.0287	—
Succinic . . . . .	.1194	.00496	.00195
Malic . . . . .	.2851	.01181	.0070
Tartaric . . . . .	.5540	.02296	.0121
Racemic . . . . .	.5540	.02296	—
Citric . . . . .	.4753	.01635	.0080

In the third column the approximate values of the true coefficients of affinity calculated from the acetamide experiments are indicated. For the stronger acids the agreement between the numbers is excellent, although the one series is for  $26^{\circ}$ , the other for  $65^{\circ}$ , and for weak acids the divergence is in the expected direction, the numbers from acetamide being always less than those from methyl acetate. The retarding action of the neutral salts is in their case so enormous (*vide infra*), that even the small quantities formed in the first period of the reaction have an important influence.

Nevertheless it is quite apparent from this comparison that we are indeed dealing in all the various chemical processes hitherto considered with the same, numerically definite, properties of acids. To the interesting relations between these and the chemical composition and constitution of the acids a special chapter will be devoted.

Cane-sugar, under the influence of free acids, is decomposed with absorption of the elements of water without the acid apparently taking any part in the process. We are not yet in a position to form any clear representation of the cause of this action as we did for the "catalytic" decomposition of methyl acetate, but the supposition is, justified that the two processes are not only externally but intrinsically quite similar. Here also it is the affinity of the acid for the alcoholic hydroxyls of the dextrose and levulose produced from the cane-sugar that acts in the predisposing fashion already indicated (p. 348), and so conditions the decomposition.

Biot, to whom we owe the fundamental observations on the process and the accompanying changes in the power of rotating the plane of polarisation, drew attention to the interest which a comparative investigation of the influence of the different acids would possess. This same process of the inversion of cane-sugar is, as already observed, that by means of which Wilhelmy in 1850 proved the fundamental law of chemical action.

Löwenthal and Lenssen (1862), endeavoured to utilise sugar-inversion for investigating the affinity of the inverting acids. Their object was "to express in numbers the magnitude of the affinities of the substances," but, although they were on the proper path for reaching this end, one can scarcely say that they altogether attained their object.

The greatest shortcoming of their research, which is indeed exceedingly rich in correctly observed facts, is the want of a measure for the reactions investigated. Although Wilhelmy twelve years previously had been perfectly cognisant of the law governing the action of acids on sugar, Löwenthal and Lenssen, evidently unaware of his work, made no attempt to find such a law at all. Their measurements are therefore, in spite of the careful execution, in the main of only qualitative character. They were able, by always making comparable experiments, to judge if an acid was stronger or weaker than another, or equal to it, but could not express the difference with numerical exactness. They also worked at the variable laboratory

temperature, so that the calculation of the inversion coefficients from their numbers, although still possible, could not be made with any great claim to accuracy.

Ostwald in 1884 employed the method extensively to determine the action of different acids. Column I of the following table contains the coefficients of inversion  $cA = \frac{1}{\theta} \log \frac{B}{B-x}$  multiplied by 10,000; column II the same with reference to hydrochloric acid = 1; in column III the coefficients of velocity for the reaction with methyl acetate are tabulated for comparison.

Acid.	I	II	III
Hydrochloric . . . . .	21·87	1·000	1·000
Hydrobromic . . . . .	24·38	1·114	·983
Nitric . . . . .	21·87	1·000	·915
Chloric . . . . .	22·61	1·035	·944
Sulphuric . . . . .	11·72	·536	·547
Ethylsulphuric . . . . .	21·86	1·000	·987
Isethionic . . . . .	20·07	·918	·978
Ethanesulphonic . . . . .	19·93	·912	·979
Benzenesulphonic . . . . .	22·82	1·044	·991
Formic . . . . .	·335	·0153	·0131
Acetic . . . . .	·0876	·00400	·00345
Isobutyric . . . . .	·0733	·00335	·00264
Monochloroacetic . . . . .	1·059	·0484	·0430
Dichloroacetic . . . . .	5·93	·271	·230
Trichloroacetic . . . . .	16·47	·754	·682
Glycollic . . . . .	·286	·0131	-
Lactic . . . . .	·233	·0107	·00901
Methylglycollic . . . . .	·397	·0182	-
Ethylglycollic . . . . .	·300	·0137	-
Methylactic . . . . .	·304	·0139	-
Diglycollic . . . . .	·583	·0267	-
Pyruvic . . . . .	1·419	·0649	·0670
Glyceric . . . . .	·375	·0172	—
Oxyisobutyric . . . . .	·232	·0106	·00921
Oxalic . . . . .	4·00	·1857	·1746
Malonic . . . . .	·674	·0308	·0278
Succinic . . . . .	·1192	·00545	·00496
Pyrotartaric . . . . .	·234	·01072	—
Malic . . . . .	·278	·0127	·0118
Citric . . . . .	·377	·0172	·0164
Phosphoric . . . . .	1·357	·0621	—
Arsenic . . . . .	1·052	·0481	—

The agreement of columns II and III again shows that the coefficients of velocity of quite different reactions caused by acids have the same value. The method of sugar-inversion ranks along with those already discussed as a mode of measuring the affinity, and surpasses most of them in this respect, that it is almost free from secondary actions.

More detailed consideration of the numerical values of the coefficients of inversion will be given in a subsequent chapter.

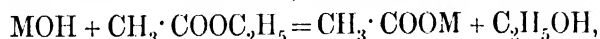
Löwenthal and Lenssen had remarked an influence of neutral salts on the action of the acids. While the diminution of the rate of inversion in the case of dibasic acids could be easily explained by the formation of acid salts, the increase in the case of the strong monobasic acids appeared inexplicable, as no reaction between these and their neutral salts had ever been betrayed by thermal or other phenomena. This influence of the neutral salts, however, is exhibited in the most general fashion, being by no means confined to the single process of inversion.

In all the methods employed the same influence has appeared, and the laws to which it is subject may be stated as follows:—All nitrates and chlorides investigated increase the action of the free acids, the influence being greatest for the potassium salts, somewhat less (and almost equal) for the sodium and ammonium salts, and least for the magnesium salts. With increasing dilution the action diminishes, and with increase of the quantity of the neutral salt the influence of the latter increases—in most cases almost proportionally.

The increase of the action of monobasic acids is nevertheless not general. It only occurs with the strongest acids, passing with weak acids into a diminution of the action which with the weakest is of extraordinary magnitude. For example, the presence of an equivalent quantity of potassium acetate reduces the action of acetic acid to one-fortieth of its proper value. The explanation of this phenomenon will be given hereafter.

The affinity of bases has hitherto scarcely been investigated, although quite similar methods seem applicable to them as are used for acids. Berthelot made some experiments on the equilibrium between soda and ammonia when contending for an acid; they led him to the result that ammonia is completely “or sensibly” displaced by the soda. Menschutkin arrived at the same conclusion by making use of the fact that phenolphthalein is coloured in alcoholic solutions by potash but not by ammonia; his results thus hold only for alcoholic solutions, and are not quite unexceptionable.

Only one kinetic method has been tested and applied—the saponification of acetic ether. R. Warder, to whom we owe the first experiments in this direction, confined himself to the observation of soda solutions, but Reicher afterwards extended the investigation to other bases. The coefficients of velocity obtained by him for the reaction



where M represents different metals, are as follows:—

Soda . . . .	2.307	Strontia . . . .	2.204
Potash . . . .	2.298	Baryta . . . .	2.144
Lime . . . .	2.285	Ammonia . . . .	.011

There is thus no great difference between the values for the alkali



and for the alkaline earths, just as the strong mineral acids have almost equal coefficients of affinity; ammonia is much weaker. In particular the numbers for potash and soda are almost identical.

Ostwald tested these results by the same method, and confirmed them as far as the strong bases are concerned, to which he found might be added lithia and thallia with nearly equal values.

With regard to ammonia, it appeared that the simple formula of p. 295, applicable to strong bases, loses its applicability in this case, for here the ammonium acetate formed in the reaction exerts a strong retarding influence. If this salt is specially added beforehand, the saponification takes place much more slowly than without the addition. As the quantity of ammonium acetate increases during the reaction, the coefficient of velocity does not remain constant but continually decreases, as is seen on calculation of the observations with the ordinary formula.

The substituted ammonias, or amine bases, behave similarly, although the retarding action in their case does not reach the same high degree as with ammonia.

This circumstance greatly enhances the difficulty of estimating the strength of these bases. We can, however, eliminate the effect of the disturbing action in the following way, without going into the somewhat complicated theory of the matter. If we calculate the coefficients of velocity in the usual manner, and tabulate those that decrease with the time as ordinates, against the time as abscissæ, we obtain a curve, in general convex to the axis of abscissæ. If we now produce this curve to cut the axis of ordinates ( $\theta = 0$ ) we obtain the coefficients of velocity for the first instant; and this is free from the disturbing action, for no acetate has then been formed. Although the process, owing to the necessary extrapolation, is not very exact, it still admits of our finding the wished-for values with a degree of accuracy sufficient for most purposes.

The following coefficients of velocity were determined in this way:—

Soda . . . . .	162	Amylamine . . . . .	18.5
Potash . . . . .	161	Allylamine . . . . .	4.0
Lithia . . . . .	165	Dimethylamine . . . . .	22
Thallia . . . . .	148	Diethylamine . . . . .	26
Ammonia . . . . .	3.0	Trimethylamine . . . . .	7.3
Methylamine . . . . .	19	Triethylamine . . . . .	22
Ethylamine . . . . .	19	Piperidine . . . . .	27
Propylamine . . . . .	18.6	Tetraethylammonium	
Isobutylamine . . . . .	14.4	hydroxide . . . . .	131

The numbers are for a dilution of 40 l. and for 25°. The substituted ammonias are all stronger than ammonia itself. We cannot, however, enter here into a detailed discussion of the results.

The tetra-substituted ammonium hydroxides behave quite differently from the amine bases. As their chemical character places them with the fixed alkalis, so does their behaviour in saponifying ethyl acetate rank them in the same class, the value obtained for tetraethylammonium hydroxide, 131, being little less than those obtained for the alkalis.

## CHAPTER IV

### ELECTROCHEMICAL RELATIONS

THE results of the investigations on chemical affinity described in the preceding chapters may all be embraced in the principle that the action of this affinity is governed by definite coefficients appertaining to the active substances and independent of the nature of the reaction. This principle is in the first instance purely empirical; there is nothing contained in it that in any way leads to a conception of the cause of such a law. Undoubtedly we can say that one and the same cause is at the bottom of all these phenomena and determines them quantitatively, but what the nature of that cause is, and what conditions the activity of the various substances—acids and bases alike—remains unknown.

The explanation came in a way not very nearly related to the modern developments of chemistry. When the electrochemical ideas of Berzelius—introduced by him from a false interpretation of his experiments, and only utilised for systematic purposes—had fallen into disrepute, the actual close connection between chemical and electrical phenomena was left entirely out of consideration. Now for the second time this connection has proved of fundamental significance, and that for the highest scientific problem of chemistry—for the question of the laws of chemical affinity.

The first indication of this new train of thought is to be found in Hittorf's observation that the mobility of the components of electrolytes, *i.e.* their power of entering into chemical reactions, is manifested in their electric conductivity. On the other hand, we have the view introduced by Williamson and Clausius that states of chemical equilibrium are stationary states, *i.e.* not of complete repose but of equal and opposite transformations. These ideas, however, were merely of a qualitative description. It was only in 1884 that Svante Arrhenius for the first time proved definite and quantitative relations to exist between electrical and chemical properties.

It has several times been shown in the preceding part of this book that a series of very dissimilar phenomena (in particular the deviations

of salt-solutions from the general laws regulating dilute solutions, and the phenomena of electrolytic conductivity) find their common explanation in the assumption that salts and like substances are in aqueous solution dissociated into their ions. The laws of chemical affinity empirically obtained above are susceptible of a similar explanation; we have only to make the additional assumption that the possibility of taking part in chemical reactions lies only in the free ions, and that consequently the capability of reaction in a given solution is proportional to the number of free ions it contains.

The fact stated by Hittorf that the power of reaction and the electrolytic conductivity are always concurrent properties, speaks at once in favour of this assumption. It obtains further support from the circumstance that the processes of electrolytic conductivity and of chemical decomposition both depend on the molecules under consideration falling into smaller submolecules; without this decomposition there can be neither a new distribution of parts, as in chemical reaction, nor a transport of the electricity attached to the ions, as in conduction.

But the most decisive and telling argument for the soundness of the assumption is the numerical agreement of the values for the chemical activity on the one hand and the electric conductivity on the other. The numbers on pp. 354 and 356 for the rate of catalysis of methyl acetate and of the inversion of cane-sugar agree so closely with those representing the relative electric conductivity, that there cannot exist the slightest doubt of the intimate connection between the two series.

In the following table there is tabulated under I the electric conductivity of normal solutions of acids, under II the coefficients of velocity for the catalysis of methyl acetate, and under III the coefficients of inversion of cane-sugar.

Acid.	I	II	III
1. Hydrochloric, $\text{HCl}$ . . . . .	100	100	100
2. Hydrobromic, $\text{HBr}$ . . . . .	100·1	98	111
3. Nitric, $\text{HNO}_3$ . . . . .	99·6	92	100
4. Ethanesulphonic, $\text{C}_2\text{H}_5\cdot\text{SO}_2\text{OH}$ . . . . .	79·9	98	91
5. Isethionic, $\text{C}_2\text{H}_4\text{OH}\cdot\text{SO}_2\text{OH}$ . . . . .	77·8	92	92
6. Benzenesulphonic, $\text{C}_6\text{H}_5\cdot\text{SO}_2\text{OH}$ . . . . .	74·8	99	104
7. Sulphuric, $\text{H}_2\text{SO}_4$ . . . . .	65·1	73·9	73·2
8. Formic, $\text{H}\cdot\text{COOH}$ . . . . .	1·68	1·31	1·53
9. Acetic, $\text{CH}_3\cdot\text{COOH}$ . . . . .	·424	·345	·400
10. Monochloracetic, $\text{CH}_2\text{Cl}\cdot\text{COOH}$ . . . . .	4·90	4·30	4·84
11. Dichloracetic, $\text{CHCl}_2\cdot\text{COOH}$ . . . . .	25·3	23·0	27·1
12. Trichloracetic, $\text{CCl}_3\cdot\text{COOH}$ . . . . .	62·3	68·2	75·4
13. Glycollic, $\text{CH}_2\text{OH}\cdot\text{COOH}$ . . . . .	1·34	—	1·31
14. Methylglycollic, $\text{CH}_2(\text{OCH}_3)\cdot\text{COOH}$ . . . . .	1·76	—	1·82
15. Ethylglycollic, $\text{CH}_2(\text{OC}_2\text{H}_5)\cdot\text{COOH}$ . . . . .	1·30	—	1·37
16. Diglycollic, $\text{O}(\text{CH}_2\cdot\text{COOH})_2$ . . . . .	2·58	—	2·67

Acid.	I	II	III
17. Propionic, $C_2H_5 \cdot COOH$ . . .	·325	·304	—
18. Lactic, $C_2H_4OH \cdot COOH$ . . .	1·04	·90	1·07
19. $\beta$ -Oxypropionic, $C_2H_4OH \cdot COOH$ . . .	·606	—	·80
20. Glyceric, $C_2H_3(OH)_2 \cdot COOH$ . . .	1·57	—	1·72
21. Pyruvic, $C_2H_3O \cdot COOH$ . . .	5·60	6·70	6·49
22. Butyric, $C_3H_7 \cdot COOH$ . . .	·316	·300	—
23. Isobutyric, $C_3H_7 \cdot COOH$ . . .	·311	·268	·335
24. Oxyisobutyric, $C_3H_6OH \cdot COOH$ . . .	1·24	·92	1·06
25. Oxalic, $(COOH)_2$ . . .	19·7	17·6	18·6
26. Malonic, $CH_2(COOH)_2$ . . .	3·10	2·87	3·08
27. Succinic, $C_2H_4(COOH)_2$ . . .	·581	·50	·55
28. Malic, $C_2H_3OH(COOH)_2$ . . .	1·34	1·18	1·27
29. Tartaric, $C_2H_2(OH)_2(COOH)_2$ . . .	2·28	2·30	—
30. Racemic, $C_2H_2(OH)_2(COOH)_2$ . . .	2·63	2·30	—
31. Pyrotartaric, $C_3H_6(COOH)_2$ . . .	1·08	—	1·07
32. Citric, $C_3H_4OH(COOH)_3$ . . .	1·66	1·63	1·73
33. Phosphoric, $PO(OH)_3$ . . .	7·27	—	6·21
34. Arsenic, $AsO(OH)_3$ . . .	5·38	—	4·81

The values for hydrochloric acid have in all three columns been made equal to 100. The agreement is not absolute, for it must be remembered that the numbers are for different concentrations. The intimate relation of the values is, however, so striking that the actual validity of the law is placed beyond doubt, and it only remains to discuss the question of how the variations from it are to be explained.

Now the assumption that the chemical activity of a substance of the type of the salts, acids, or bases, is proportional to the number of their molecules split up into free ions, makes clear the existence of specific coefficients of affinity, dependent only on the nature of the substance and not on the nature of the reaction. There is not, as was formerly for the most part imagined, a special force active between the reacting particles, but the measure of the activity is given by the number of electrolytically dissociated ions, no matter on what these ions may in the specified case react.

We must, therefore, conclude that all acids, for instance, would be equally strong if fully dissociated. Now the dissociation increases with the dilution according to laws to be given presently; acids already tolerably far dissociated at moderate dilutions will not gain much in dissociation and strength by further dilution; acids but little dissociated must, on the other hand, grow rapidly stronger as the dilution increases. On comparing the numbers on p. 346 for 1 l. and 10 l. we see that this is indeed the case.

There must further be a maximum of chemical activity corresponding to complete dissociation and not capable of being exceeded by any acid. Hydrochloric acid at moderate dilutions is very near this maximum. It has not been found that any acid exceeds hydrochloric acid in strength to any considerable extent; no sort of com-

bination of "negative" atoms, such as may be found in chloric acid,  $\text{HClO}_3$ , methanedisulphonic acid,  $\text{CH}_2(\text{SO}_3\text{H})_2$ , or pentabrom-benzene-sulphonic acid,  $\text{C}_6\text{Br}_5 \cdot \text{SO}_3\text{H}$ , shows an action in any way more powerful than is exhibited by hydrochloric acid.

It only remains to bring these somewhat qualitative relations into the form of quantitative laws. If electrolytes are actually dissociated, the same laws must hold for this state of dissociation as we found to apply to gases. Let us consider in the first place binary electrolytes, of which each molecule falls into one positive and one negative ion; we have then (if  $u$  is the number of original,  $w$  of decomposed molecules in unit volume) the following condition for equilibrium

$$cu = c'w, w = c'w^2,$$

for from each original molecule we obtain two on decomposition.

The number of decomposed molecules is, according to what was stated on p. 285, proportional to the molecular conductivity. If we call this  $\mu$  for some finite dilution, the fraction  $\frac{\mu}{\mu_\infty}$  gives the proportion of molecules decomposed,  $\mu_\infty$  being the limit of electric conductivity for infinite dilution and complete dissociation. The complement of this number,  $1 - \frac{\mu}{\mu_\infty}$ , is consequently the proportion of molecules undecomposed.

Now the active quantity of the two portions is the absolute amount divided by the volume  $v$ ; we can thus write  $u = \frac{1}{v} \left(1 - \frac{\mu}{\mu_\infty}\right)$  and  $w = \frac{1}{v} \cdot \frac{\mu}{\mu_\infty}$ . Introducing these values in the above equation we obtain

$$\frac{c}{v} \left(1 - \frac{\mu}{\mu_\infty}\right) = \frac{c'}{v^2} \left(\frac{\mu}{\mu_\infty}\right)^2,$$

or on transformation

$$\frac{\mu^2}{v\mu_\infty(\mu - \mu_\infty)} = \frac{c}{c'} = k.$$

Lastly, if we make the ratio  $\frac{\mu}{\mu_\infty}$  equal to  $m$ , *i.e.* if we refer the molecular conductivity to the limiting value as unity, we get

$$\frac{m^2}{v(1 - m)} = k.$$

It is thus to be expected that the influence of the dilution  $v$  on the molecular conductivity of binary electrolytes will be represented by this equation.

This expectation is realised in the most complete manner. Ostwald (1889) found the formula to agree with experiment for over two hundred acids.

From the form of the equation the following conclusions can at once be drawn. The constant  $k$  is dependent on the nature of the substance, but we can always choose states of dilution  $v_1$  and  $v_2$  for two different substances so that the products  $v_1 k_1$  and  $v_2 k_2$  shall be equal. In that case  $\frac{m^2}{1-m}$ , and consequently  $m$ , must be the same for both, *i.e.* the conductivity with reference to the limiting value, or, what is the same thing, the proportion of dissociated molecules is for both substances the same. If we alter both dilutions in the same ratio, double them for example, the products  $v_1 k_1$  and  $v_2 k_2$  are still equal, and so also must be the values of  $m$ . From this it follows that the dilutions at which two substances are dissociated to the same extent are always proportional, independent of the absolute values of the dilution. This law was empirically discovered by Ostwald (1885) for relative molecular conductivity before he had applied the theory of dissociation to electrolytes.

If the value of  $m$  is very small, then  $1-m$  differs but little from unity and undergoes only small alteration with increase of the dilution. The equation then assumes the form

$$\frac{m^2}{v} = \text{const.}$$

The conductivity is proportional to the square root of the dilution. Kohlrausch (1878) deduced this law empirically from his measurements on acetic acid and ammonia, and it afterwards received from Ostwald the most ample confirmation.

The severest test of the formula is to determine  $m$  for a number of different dilutions and then calculate from the values obtained the constant  $k$ , which ought to be independent of the dilution. The following numbers were observed for acetic acid:—

$v$	$\mu$	$m$	$k$
8	4.34	.0119	.0000180
16	6.10	.0167	179
32	8.65	.0238	182
64	12.09	.0333	179
128	16.99	.0468	179
256	23.82	.0656	180
512	32.20	.0914	180
1024	46.00	.1266	177

Under  $v$  we have the dilution in litres per gram-molecular-weight, under  $\mu$  the molecular conductivity in mercury units, and under  $m$  the same referred to the maximum  $\mu_\infty = 364$ . The calculation of this maximum value is made as indicated on p. 285, the velocity of migration of the acetion,  $\text{CH}_3\text{CO}_2$ , being determined from the conductivity of the sodium salt, and to it being added the corresponding velocity of hydrogen. From each measurement we obtain a value for

k, and we see that these numbers lie so close round the mean value  $k = .0000180$ , that the unavoidable error of experiment need only be taken into account to explain any slight deviations.

What was found for acetic acid is confirmed in the same way for all other monobasic acids investigated, so that the law is quite general. Only with such acids as are very near the maximum value is the constant k not accurately calculable; for them, the slightest error in the determination of the conductivity conditions a great variation in the value of k.

Knowing the constant k we can calculate the conductivity, and thus also the chemical activity of an acid for any dilution. We have only for this purpose to solve the equation for m, when we obtain

$$m = \frac{-vk + \sqrt{v^2k^2 + 4vk}}{2}$$

We have, hitherto, spoken of monobasic acids only. When the values of the constant are small, polybasic acids behave in respect of conductivity exactly as monobasic acids. From this it is apparent that the dissociation does not, as we might at first expect, affect the hydrogen atoms of the two carboxyl groups simultaneously, but that first only one of them is split off. If, therefore,  $H_2A''$  is the formula of a dibasic acid, the electrolytic dissociation takes place according to the scheme  $H \mid H_2A''$ , and not according to the scheme  $H_2 \mid A''$ . Only when the dissociation has gone a considerable length does the second hydrogen atom begin to separate; in most cases this does not happen in any marked degree until at least half of the molecules have decomposed in the sense  $H \mid H_2A''$ . We may take succinic acid as an example. The signification of the letters is as in the preceding table.

v	$\mu$	m	k
16	11.40	.0320	.0000662
32	16.03	.0450	662
64	22.47	.0632	667
128	31.28	.0880	664
256	43.50	.1224	668
512	59.51	.1675	659
1024	81.64	.2295	668
2048	109.5	.3082	671

The value 356 has been taken for  $\mu_\infty$ . The constant k proves to be the same for all the dilutions, which vary in the proportion of 1 to 128. It should be mentioned that such a comprehensive confirmation of the law of dissociation for gases has never yet been obtained.

If the polybasic acids are stronger, the formula for monobasic acids no longer holds good. In the solutions we have then molecules H,  $HA''$ , and  $A''$ , forming a somewhat complicated equilibrium with each other, the calculation of which cannot here be given. Very strong dibasic acids whose solutions contain, for the most part, 2H and

A'', are similar to the strongest monobasic acids, the molecular conductivity changing little with the dilution. The maximum lies about twice as high as for monobasic acids.

Similar considerations apply to tribasic and polybasic acids.

If, from the point of view we have now reached, we look at the facts discussed in the preceding chapter, we can easily understand why the state of dissociation or the number of free and active ions determines the velocity of such processes as the inversion of sugar, the catalysis of methyl acetate, or the decomposition of acetamide. In these cases there are present in the liquid besides the active electrolytic substance only non-electrolytes, or at least such bodies as are decomposed electrolytically only to a vanishingly small extent, so that the active substance can freely exert its influence.

The circumstances are different when several electrolytes are present in the liquid at the same time. The question must then be settled if the state of dissociation of each electrolyte is independent of the other or not. We can at once dispose of one case, that, namely, of all the electrolytes in the solution being fully dissociated or nearly so. They can then no longer influence each other, and the laws obtaining for the separate solutions may be applied to the mixture.

But if a highly dissociated and a weakly dissociated substance be simultaneously present in the solution, there will be mutual influence, if both contain one common ion. The formulæ of chemical equilibrium for quantities not equivalent then apply, and the state of equilibrium is different.

If we ask how two solutions must be constituted in order that the dissolved and partially dissociated substances may not influence each other, we must first of all claim that the active mass of the components shall not alter on mixing. Two solutions of the same substance will therefore not influence each other when their concentrations are equal, as indeed is *a priori* perfectly clear. The question is somewhat more complicated for two different substances containing a common ion, *e.g.* two acids. We shall consider for simplicity's sake two monobasic acids HA<sup>1</sup> and HA<sup>2</sup>. According to the general formulæ for chemical equilibrium these two equations will hold good—

$$c_1 \frac{1 - \xi_1}{v_1} = c_1' \frac{\xi_1}{v_1} \cdot \frac{\xi_1}{v_1}$$

$$c_2 \frac{1 - \xi_2}{v_2} = c_2' \frac{\xi_2}{v_2} \cdot \frac{\xi_2}{v_2},$$

where  $\xi$  is the dissociated portion and  $v$  the volume containing a gram-molecular-weight.

If we mix the two solutions, the volume becomes  $v_1 + v_2$ . The concentrations of the undecomposed portions fall to  $\frac{1 - \xi_1}{v_1 + v_2}$  and



$\frac{1 - \xi_2}{v_1 + v_2}$ , while those of the acid ions fall to  $\frac{\xi_1}{v_1 + v_2}$  and  $\frac{\xi_2}{v_1 + v_2}$ , and that of hydrogen becomes  $\frac{\xi_1 + \xi_2}{v_1 + v_2}$ . The equations of equilibrium for the two acids are thus

$$c_1 \frac{1 - \xi_1}{v_1 + v_2} = c_1' \frac{\xi_1}{v_1 + v_2} \cdot \frac{\xi_1 + \xi_2}{v_1 + v_2}$$

$$c_2 \frac{1 - \xi_2}{v_1 + v_2} = c_2' \frac{\xi_2}{v_1 + v_2} \cdot \frac{\xi_1 + \xi_2}{v_1 + v_2}$$

If we divide each of these into the corresponding equation of the upper pair we obtain after a little easy simplification

$$\frac{\xi_1}{\xi_2} = \frac{v_1}{v_2} \quad \text{or} \quad \frac{\xi_1}{v_1} = \frac{\xi_2}{v_2}$$

Thus, in order that the states of dissociation of two acids be not altered on mixing, the dissociated portions must be as the dilutions. Or, according to the second form of the equation, the concentration of the hydrogen ions must be the same in both solutions.

Thus if we have acetic acid for example, which is only slightly dissociated, and hydrochloric acid, which is highly dissociated, we must take very dilute solutions of the latter and moderately strong solutions of the former to get the same concentration of the hydrogen ions. From the table on p. 363 we see that acetic acid contains in round numbers .012 equivalents of hydrogen as free ions for a dilution of 8 l.; the concentration with respect to this ion is therefore  $\frac{.012}{8} = .0015$ . Hydrochloric acid will be without influence on this solution when the concentration of its hydrogen corresponds to the equation  $\frac{\xi}{v} = .0015$ . Since it may be considered completely dissociated at the requisite great dilutions, we have  $\xi = 1$  and consequently  $v = 667$ . The hydrochloric acid must therefore be of the concentration of one gram-equivalent in 667 litres.

Arrhenius, to whom the foregoing considerations are due (1888), terms such solutions as do not mutually alter their state of dissociation isohydric. Since according to the formula just developed it is only necessary for this that the concentrations of the same ion be equal, the absolute quantities of the solutions or their ratio playing no part, it follows that isohydric solutions leave each other undisturbed no matter in what proportions they may be.

Hence we conclude what will happen when two solutions not isohydric are mixed; they will so act on each other that they become isohydric. If we imagine the two solutions to be placed first in layers one above the other, we can remove water from the solution in which the concentration of the common ion is the smaller, and give it to the

other solution, and go on doing so until the concentration in the two solutions has become the same. They are then isohydric, and can be mixed without any change in either taking place.

The removal of water has a twofold action. In the first place, the concentration increases proportionally to the amount of water removed. But this is not all,—the dissociation is diminished because the volume is smaller, and so the concentration of ions is less. Now the first action has the preponderance, for it is proportional to the quantity of water, while the second is at most proportional to the square root of this quantity; but in any case the calculation is hereby complicated. The same thing holds for the solution to which water is added: the concentration of the common ion decreases on account of the increased dilution, which, however, determines an increase of the dissociation, and so the diminution is smaller than would be calculated from the dilution alone.

Two solutions isohydric with a third are isohydric with each other. For if two solutions are isohydric with a third, they each contain one ion at the same concentration as in the third, and thus have the same concentration themselves and are isohydric. This theorem was discovered experimentally before the theory showed it to be necessary.

It should particularly be noted that this law only holds for such solutions as contain a common ion; if no common ion is present the matter assumes a different shape, and to the consideration of this case we shall now turn.

As was formerly remarked, solutions of almost all salts are highly dissociated, and also those of the strong mineral acids. If we mix a dilute solution of hydrochloric acid, which contains the free ions H and Cl almost exclusively, with a dilute solution of a salt, which we may denote generally by MA, M being the metal and A the acid radical,—then for equilibrium it is necessary that all positive and negative ions should be in dissociation-equilibrium with respect to the possible compounds. Should the acid of the salt in the free state be likewise highly dissociated, equilibrium between the hydrogen of the hydrochloric acid and the acid radical A will be also approximately existent. If, however, the acid HA is only dissociated to a very slight extent, like acetic acid, the hydrogen of the hydrochloric acid and the acid radical will act on each other so as to form undissociated molecules HA until the remaining hydrochloric acid becomes isohydric with the acid HA formed. The result is thus that a certain quantity of the acid HA is formed at the expense of the salt MA and the hydrochloric acid, the amount being greater the less the acid is dissociated, *i.e.* the weaker it is.

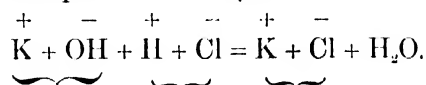
This in the light of the theory of dissociation is the process hitherto known as the displacement of a weak acid from its salt by a stronger acid, and ascribed to a special chemical force of affinity

between the metal and the various acid radicals. We see that the cause lies in the nature of the acid; the metal of the salt plays but a small part, for it only serves by its presence to keep the ion of the acid in the dissociated state. Thus is explained the empirical law (p. 342) that the ratio in which one acid is "displaced" from a salt by another does not depend on the nature of the basic component.

We must now conceive another process in the same way, for which also a sort of action at a distance has been hitherto made accountable,—namely, the neutralisation of an acid by a base. If, as we have often stated, a salt is dissociated into its two ions, it appears at first sight incomprehensible why an acid and a base should act on each other in any way, since their two active components, the metal and the acid ion, do not enter into combination with each other at all.

This is perfectly correct, however; salt-formation in aqueous solution is in reality not a combination of these components of acid and base, but consists in the combination of the two other components, the hydrogen of the acid with the hydroxyl of the base. Water is an electrolyte of extraordinarily small dissociation, as is seen from its excessively slight conductivity,—although at the same time the ions, OH and H, have specially great velocities of migration. Consequently it is impossible for the ions hydrogen and hydroxyl to exist uncombined in the same liquid, and so when they meet they immediately unite to form water. The process of neutralisation in aqueous solution is thus nothing but a formation of water.

The simplest case is when a strong acid acts on a strong base, as we have then only to consider substances for the most part dissociated. The formation of potassium chloride from potash and hydrochloric acid would thus correspond to the equation



If this conception is correct the heat of neutralisation of such powerful acids and bases must be independent of the nature of the substances and possess in fact a constant value representing the heat of combina-

tion of  $\overset{+}{\text{H}}$  and  $\overset{-}{\text{OH}}$  to form water. It has already been shown that this is actually the case, the development of heat on the action of hydrochloric, hydrobromic, hydriodic, nitric, chloric, perchloric, iodic, ethylsulphuric, the sulphonic acid, etc., on strong bases like potash, soda, lime, baryta, strontia, or tetramethylammonium hydroxide being always very nearly the same, viz. 137 or 138 K.

If one of the components (or both) is in a less dissociated condition, there must be added to the heat of formation of the water the heat of dissociation of the substance in question, as in order to produce hydrogen or hydroxyl (or both) for the formation of water it is

necessary that it should first fall into its ions. Deviations from the number 137-138 K are therefore only possible for the weaker acids and bases. This law also is in complete accordance with experiment. The greatest divergence is shown in the case of hydrofluoric acid and phosphoric acid; both are weak acids and feebly dissociated. From the fact that their heat of neutralisation is greater than 137 it appears that heat is liberated on their dissociation, which must therefore diminish with rise of temperature. Sulphuric acid too in the solutions employed by Thomsen is only dissociated to the extent of 50-60 per cent, so that its somewhat high heat of neutralisation can be explained in the same way.

Finally, on the basis of these considerations it is easy to perceive the cause of Favre and Silbermann's law of constant differences in the heat of neutralisation (p. 219) as well as of Hess's Law of Thermo-neutrality. The heats of neutralisation can be represented as sums of a constant term, a term depending on the base, and a term depending on the acid. This must be so, for the heat of neutralisation is composed of

- (a) the heat of dissociation of the acid,
- (b) the heat of dissociation of the base,
- (c) the heat of formation of water.

The term a depends only on the nature of the acid, b only on the nature of the base, and c is constant, *i.e.* independent of both.

This conception of the chemical process of neutralisation may, at first sight, appear somewhat strange and opposed to the customary views. It has, however, the great advantage of resting on a broader empirical foundation, and besides, of explaining and connecting together phenomena which the ordinary more or less vague ideas either leave without explanation, or acknowledge to be contradictory.

It should be mentioned that the other physical and chemical phenomena accompanying neutralisation, in particular the change of volume, of refraction, etc., are capable of being explained in the same way, but it is scarcely necessary to enter into the details.

We must now fix quite generally the conditions for the establishment of chemical equilibrium between four substances, which can be formed by the combination in pairs of two negative and two positive ions. These conditions may be expressed in the following theorem:— If isohydric solutions of  $A_1B_1$ ,  $A_1B_2$ ,  $A_2B_1$ ,  $A_2B_2$  be prepared ( $A_1B_1$  being made isohydric with  $A_1B_2$ , this with  $A_2B_2$ , and this again with  $A_2B_1$ ), then when these are mixed in such volumes a, b, c, d that the equation

$$ad = bc$$

holds good, the substances are and will remain in equilibrium.

If we denote the undissociated quantities of the four substances by  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , and remember that the dissociated portions are proportional to the volumes (for according to hypothesis the solutions are

isohydric), and can thus be denoted by  $ha$ ,  $hb$ ,  $hc$ ,  $hd$ , where  $h$  is a constant, then the equations for equilibrium will be as follows:—

$$k_1 \frac{a}{a} = k_1' \left( \frac{ha}{a} \right)^2, \quad k_2 \frac{\beta}{b} = k_2' \left( \frac{hb}{b} \right)^2, \text{ etc.}$$

or  $k_1 a = k_1' h^2 a, \quad k_2 \beta = k_2' h^2 b, \text{ etc.}$

If we now imagine the four volumes  $a$ ,  $b$ ,  $c$ ,  $d$  to be mixed, new conditions of equilibrium will appear, the equations assuming the following form:—

$$k_1 \frac{a}{a+b+c+d} = \frac{k_1' h^2 (a+b)(a+c)}{(a+b+c+d)^2},$$

$$k_2 \frac{\beta}{a+b+c+d} = \frac{k_2' h^2 (b+a)(b+d)}{(a+b+c+d)^2}, \text{ etc.}$$

For in the mixture the undissociated quantity of  $A_1B_1$  is as before  $a$ , but it is now contained in the volume  $a+b+c+d$ . Of the dissociated portions  $A_1$  and  $B_1$  the quantity  $a$  of  $A_1$  comes from the solution  $A_1B_1$  and the quantity  $b$  from the solution  $A_1B_2$ ; of  $B_1$  we have  $a$  from  $A_1B_1$  and  $c$  from the third solution  $A_2B_1$ ; each quantity must again be divided by the total volume in order that the concentration may be obtained. The other equations follow in a similar manner.

On reduction they give—

$$k_1 a = \frac{k_1' h^2 (a^2 + ab + ac + bc)}{a+b+c+d}; \quad k_2 \beta = \frac{k_2' h^2 (b^2 + ab + bd + ad)}{a+b+c+d}, \text{ etc.}$$

Now, in order that the state of dissociation of the four substances shall be unchanged it is necessary that the relations between  $a$  and  $\alpha$ ,  $b$  and  $\beta$ , etc., remain as in the original equations. From these and the above equations we obtain by division—

$$a = \frac{a^2 + ab + ac + bc}{a+b+c+d}; \quad b = \frac{b^2 + ad + bd + ad}{a+b+c+d}, \text{ etc.}$$

whence

$$ad = bc; \quad ad = bc, \text{ etc.}$$

*I.e.* in order that the state of dissociation may remain unaltered the condition

$$ad = bc$$

must be fulfilled.

But the volumes  $a$ ,  $b$ ,  $c$ ,  $d$ , are proportional to the active or dissociated portions of the various electrolytes,  $a$  and  $d$  belonging to the substances  $A_1B_1$  and  $A_2B_2$ , which by their mutual action give  $A_1B_2$  and  $A_2B_1$ . The dissociated quantities are again proportional to the total quantities  $p$ ,  $q$ ,  $p'$ , and  $q'$ , each multiplied by the respective factor of dissociation,  $m_1$ ,  $m_2$ ,  $m_3$ ,  $m_4$ . Consequently we get the following formula for equilibrium:—

$$m_1 p \cdot m_2 q = m_3 p' \cdot m_4 q'$$

This is not only a representation of Guldberg and Waage's law of the action of mass (p. 298), for which we put  $m_1m_2 = c$  and  $m_3m_4 = c'$ , but it also contains the extension discovered by Ostwald that each of the coefficients  $c$  and  $c'$  falls into two factors, one of which depends only on the acid, and the other only on the base, or, more accurately, one only on the positive ion and the other only on the negative ion.

The equation, however, goes beyond this empirical relation. It shows that the coefficients  $m_1m_2$  . . . which in the former equations were, as a first approximation, looked upon as constant, are in fact not so. The coefficients of dissociation depend not only on the nature of the substances themselves, but also on the presence of other substances containing the same ion, and from this last circumstance are subject to considerable variation. In this we find the explanation of the various exceptions from the law of the action of mass in the form containing the two coefficients as constants.

If all the substances taking part in the reaction are highly dissociated, the presence of the other substances has no notable influence on the state of dissociation of the several bodies. If slightly dissociated substances, on the other hand, are present, their dissociation is diminished the more the smaller it already is. We thus see that weak acids or bases in presence of their neutral salts (always rather highly dissociated) must be much weaker in their action than when they act alone. This fact also had been established empirically long before its explanation was given. A detailed investigation of the subject would take us far beyond the limits of this book. It should only be stated that so far as the results of the theory of isohydric solutions have been developed, the agreement with observed facts has been of the most satisfactory nature.

## CHAPTER V

### INFLUENCE OF THE NATURE, COMPOSITION, AND CONSTITUTION OF SUBSTANCES ON THEIR AFFINITY

THE conception of a chemical element was, up to about the time of Robert Boyle, not that of a substance, but of a property or plexus of properties, so that the presence of an element in a substance was recognised in the possession by that substance of a certain property.

In the course of the later development of chemistry this conception was replaced by another, and by chemical elements came to be understood the undecomposed residues of natural substances. On the assumption that the elements as such continued to exist in compounds, their distribution only being varied, there remained the theoretical necessity of believing that in these compounds the properties of the elements, in particular their mass, continued in existence also. We saw at the very outset how exactly this assumption is justified by the facts.

The question of course soon presents itself: What are these "essential" properties still to be found in the compounds? Evidently they are such as are connected with the substance of the elements and independent of the distribution. These properties accompany the elements in their compounds and assume values in the latter represented by the sums of the values pertaining to the elements. In a word they are the additive properties.

No strictly additive property is known save mass. The specific heat of solids has this character very nearly; to a less extent it is possessed by the refractive power and the volume of organic bodies. Here already we meet with the second circumstance that in the most decided way determines other properties, such as colour, melting and boiling points, crystalline form, etc.—the arrangement of the elements in compounds. We have already named the properties determined by the joint influence of the nature and arrangement of the elements constitutive. The extreme is formed by properties no longer depending on the nature of the elements at all but only on their distribution; these we have termed colligative.

To which group does the affinity—the capacity of the elements to exert chemical action—belong? Evidently to the constitutive group; for our daily experience shows that both the nature and what we call the arrangement of the elements is of influence. Acetic acid, lactic acid, and glucose, contain the same elements in the same proportions by weight, but they exhibit quite different capacity for chemical reaction. Butyric acid and acetic ether have not only the same composition but the same molecular weight, yet their affinities are completely different.

This shows that the distribution of the atoms has the greatest influence on the affinity; on the other hand, that the affinity depends on the nature of the elements scarcely needs illustration. Oxygen derives its name from its capability to endow substances in which it is contained with an acid character, provided that these substances are so composed that they can act as acids at all.

In seeking the regularities which govern the affinities of substances, we first of all consider the elements. It was observed in the discussion of the periodic system (p. 37) that the power of elements to form acids or bases, and to unite with various other definite elements, is subject to perfectly regular changes. These relations are unfortunately only qualitative for the most part, so that it is not yet possible to establish set numerical laws for them. It is true that attempts have been made in this direction, but the results as yet obtained are open to doubt.

We are somewhat more advanced with respect to chemical compounds. There are numerous and comprehensive researches by Menschutkin (since 1879) on the formation of esters from organic acids and alcohols, which have yielded regular results, at least for limited groups of homologous and analogous compounds. Thus the normal primary alcohols (with the exception of methyl alcohol) are esterified at the same rate; the primary alcohols not normal, and the unsaturated alcohols, more slowly; the secondary alcohols more slowly still, there being in addition differences within this last group. If the same alcohol is allowed to act on different acids, it is found that the primary fatty acids exhibit a decreasing velocity with increasing molecular weight. The secondary acids act more slowly, and the tertiary acids slowest of all.

The results of the foregoing experiments cannot be given more exactly than has been done above, as only the direct measurements of the amounts decomposed in unit time have been ascertained, and not the coefficients of velocity calculable from them. Still these investigations are of great importance in so far as they were among the very first to direct attention to actions of affinity susceptible of quantitative determination, though not yet expressed in a general measure, and to their dependence on the composition and constitution of the bodies investigated.

A research based on a well-defined measure of affinity determinable



with numerical exactness only became possible, when, by the development of the electrolytic theory of dissociation the formula was found from which a constant of a general character and independent of the dilution could be calculated. This constant has a claim to serve as the measure of affinity. As was shown in the preceding chapter the chemical activity (at all events in such processes as involve acids, bases, and salts) is measured by the degree of dissociation, which, however, depends on the dilution according to the formula

$$\frac{m^2}{1-m} = kv.$$

The formula contains a single constant  $k$ , determined by the nature of the substance, and this constant is the required measure of chemical affinity.

To grasp its significance let us imagine half of the substance to be dissociated. Putting  $m = .5$  we get

$$\frac{1}{2} = kv; \quad 2k = \frac{1}{v}.$$

$2k$  is thus equal to the reciprocal of the volume, *i.e.* to the concentration, for which the electrolyte is exactly half dissociated.

The measurement of electric conductivity is the simplest and most exact method of measuring  $k$ . We have seen (p. 362) that the extent of dissociation  $m$  is the ratio between the corresponding molecular conductivity  $\mu$  and the limiting value of the conductivity for infinite dilution,  $\mu_\infty$ .

In the short time which has elapsed since the establishment of these relations, it has not been possible to answer the questions pressing for solution with any degree of completeness. The constant  $k$  in its dependence on the composition and constitution of organic acids has alone formed the subject of investigation, for here there was the immediate possibility of collecting abundant material for comparison. The measurements made by Ostwald (1889) on some 240 acids have brought to light quite a number of regularities, which in part at least admit of a deeper insight into the nature of chemical compounds than the methods hitherto employed have enabled us to obtain.

The following pages contain an account of the most important results of the experiments. As the constant derived from the

formula  $\frac{m^2}{(1-m)v} = k$  is inconveniently small, the larger number

$K = 100k$  will be used in what follows; the relations between the different substances remain of course quite unaffected by this. All the numbers were determined from the molecular conductivities at 25°.

The constants for the fatty acids were found to be

	Acid.		K.
Formic . . . . .		H. CO <sub>2</sub> H	·0214
Acetic . . . . .		CH <sub>3</sub> . CO <sub>2</sub> H	·00180
Propionic . . . . .		C <sub>2</sub> H <sub>5</sub> . CO <sub>2</sub> H	·00134
Butyric . . . . .		C <sub>3</sub> H <sub>7</sub> . CO <sub>2</sub> H	·00149
Isobutyric . . . . .		C <sub>3</sub> H <sub>7</sub> . CO <sub>2</sub> H	·00144
Valerianic . . . . .		C <sub>4</sub> H <sub>9</sub> . CO <sub>2</sub> H	·00161
Caproic . . . . .		C <sub>5</sub> H <sub>11</sub> . CO <sub>2</sub> H	·00145

The values of the three first members decrease continuously; the substitution of CH<sub>3</sub> for hydrogen thus lowers the activity of the acids. After the third member the values vary irregularly by small amounts. The substitution therefore when taking place at a distance from the carboxyl group exerts no noticeable influence on the latter: other influences then come into play, but these are at present beyond our knowledge.

It is somewhat remarkable that the isomeric butyric and isobutyric acids should have values almost equal. This is not of frequent occurrence, isomeric compounds having mostly very diverse values.

If we introduce chlorine into acetic acid in place of hydrogen, the constant is considerably raised.

	Acid.	K.
Acetic . . . . .		·0018
Monochloracetic . . . . .		·155
Dichloracetic . . . . .		5·14
Trichloracetic . . . . .		121

Inquiring into the manner in which changes in the complex affect the carboxyl and thus the constant, we may first of all ask whether the latter is altered by the same amount or in the same ratio by the changes. A glance at the numbers is sufficient to show that the latter alternative only is possible. The differences for the substitution of one atom of hydrogen by chlorine are ·153, 4·99, and 116, while the corresponding ratios are 86, 33·2, and 23·5. That the last numbers are not equal is not surprising, for the changes are not equal, chlorine in the first case entering a molecule in which no chlorine is already present, while in the second case the substitution is effected in the group CH<sub>2</sub>Cl, in the third case it is in the group CHCl<sub>2</sub>. The three changes are thus not the same but only similar, and the ratios corresponding are consequently not equal but only of the same order.

The influence of the substituent chlorine on the acid properties of acetic acid is very considerable; we must therefore attribute to it important "acidifying" properties. The way in which this action is exerted can at present scarcely be indicated even hypothetically. Berzelius assumed that the atoms of chlorine were charged with a somewhat large excess of negative electricity and therefore exerted

a strong attraction on positively charged bodies, like the metals. This hypothesis is difficult to reconcile with the knowledge we now possess of the behaviour of electricity. No other, however, has as yet been developed. We still retain from the old theory the designation of the elements as positive or negative according as they incline to form basic or acid compounds, and this we shall continue to use in the sequel where it is not likely to produce any misunderstanding.

If instead of chlorine we take some other "negative" substituting radical, we in the same way obtain an increase in the strength of the acid. Thus, for example, we have

Acid.		K.
Acetic	$\text{CH}_3 \cdot \text{CO}_2\text{H}$	·0018
Monobromacetic	$\text{CH}_2\text{Br} \cdot \text{CO}_2\text{H}$	·138
Cyanacetic	$\text{CH}_2(\text{CN})\text{CO}_2\text{H}$	·370
Sulphocyanacetic	$\text{CH}_2(\text{SCN})\text{CO}_2\text{H}$	·265
Carbamylthioglycollic	$\text{CH}_2(\text{S} \cdot \text{CO} \cdot \text{NH}_2)\text{CO}_2\text{H}$	·0246
Thioglycollic	$\text{CH}_2(\text{SH})\text{CO}_2\text{H}$	·0225
Glycollic	$\text{CH}_2(\text{OH})\text{CO}_2\text{H}$	·0152

The constant for bromacetic acid ·138 is not very different from that for chloracetic acid ·155, as we might expect from the agreement between hydrobromic and hydrochloric acids. On the other hand, the constant of cyanacetic acid is considerably greater: cyanogen is thus a much more "negative" substituent than chlorine or bromine. Nevertheless hydrogen cyanide is so weak that it scarcely deserves the name of acid. This circumstance forces us to the conclusion that hydrogen cyanide is not at all comparable with the halogen hydracids, but is probably to be conceived as an imido-compound.

The radical sulphocyanogen is likewise of much greater influence than chlorine; but the constant does not reach the value for cyanacetic acid. Sulphocyanic acid is a genuine hydracid, and quite comparable with hydrochloric acid in point of strength.

The extraordinary enfeeblement suffered by this acid on taking up the elements of water to form carbamylthioglycollic acid, a substituted acetic acid in which the residue of thiocarbamic acid replaces a hydrogen atom, is very remarkable. The constant sinks to a tenth of its former value. The cause is probably to be sought in the action of the basic group  $\text{NH}_2$ , amidogen, which is introduced.

The replacement of the hydrogen of acetic acid by hydroxyl also conditions a considerable rise in the strength of the acid, the constant of glycollic acid being some eight times greater than the constant of acetic acid. Hydrosulphyl,  $\text{SH}$ , in the same position occasions a somewhat greater increase than hydroxyl; as we might expect from hydrogen sulphide being a stronger acid than water.

If a second hydroxyl is introduced into acetic acid, glyoxylic acid is produced.

Glyoxylic acid	$\text{CH}(\text{OH})_2\text{CO}_2\text{H}$	·0474
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The ratio between acetic and glycollic acids is 1 : 8 ; between the latter and glyoxylic acid 1 : 3. The second substitution of hydroxyl is thus less effective than the first. This result may be compared with the corresponding one for substitution of chlorine; there we found the ratios to be 1 : 86 and 1 : 33, which are related to each other exactly as the ratios of the oxyacids.

With thioglycollic acid we may compare thioacetic acid. We have—



while the constant for thioglycollic acid is ·0225, not so much as half. The reason lies in the much closer connection in thioacetic acid between the entrant “negative” sulphur atom and the acid hydrogen atom, the action of the sulphur coming much more strongly into play.

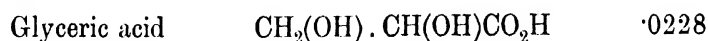
The hydroxypropionic acids are quite parallel to the corresponding derivatives of acetic acid. We have two monohydroxy-acids however, and these have different constants.

Acid.		K.
Propionic . . . .	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$	·00134
Lactic . . . . .	$\text{CH}_3 \cdot \text{CH}(\text{OH})\text{CO}_2\text{H}$	·0138
$\beta$ -Oxypropionic . . .	$\text{CH}_2(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$	·00311

While the hydroxyl in the  $\alpha$ -position increases the constant of propionic acid tenfold, the same radical in the  $\beta$ -position only acts with the factor 2·3. This is a very clear case of the general principle that the action of the various elements on the affinity depends not only on their nature, but also on their “position.” It is not a great step to take this last expression—hitherto used more in a figurative sense—literally. It is true that by doing so we enter the domain of hypothesis; but it is the already quite familiar ground of the atomic hypothesis; if we once assume discrete material particles we must allot them position in the molecular structure.

Exception has been taken to this conclusion on the ground that according to all we know of the nature of the atoms in molecules, or are justified in suspecting, these atoms are by no means at rest, but are probably in a state of brisk motion. This we must undoubtedly grant; but it should be added that the movements must be of very limited range. If they were so considerable as to make a distinction between the positions of the  $\alpha$  and  $\beta$ -hydroxyl unjustifiable, then the corresponding isomers should exhibit no chemical difference; in fact the existence of isomeric bodies would be impossible. At high temperatures both the translatory and intramolecular motions become more violent; and it is known that then isomeric compounds can often change into each other.

If a  $\beta$ -hydroxyl is introduced into lactic acid, glyceric acid is the product.



The ratio of the constant to lactic acid is 1·7, while the ratio between propionic acid and  $\beta$ -oxypropionic acid is 2·3. The alteration is in both cases of the same order, but smaller where the substituting radical is already present. This is exactly what we found for the chlorine and hydroxyl substitution products of acetic acid.

A similar influence of the position of the substituent is seen in the case of levulinic acid.

Levulinic acid       $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$       ·00255

Apart from the position of the carbonyl group this acid is related to valerianic acid as glyoxylic acid is to acetic acid. The ratio of the former acids is, however, only 1·5 : 1, while the ratio between the latter is 26 : 1. The enormous difference can only be ascribed to the distance of the oxygen atom (or the equivalent to hydroxyls) from the carboxyl in levulinic acid.

Further examples of the influence of position are to be found in the following substances :—

Acid.		K.
$\beta$ -Iodopropionic	$\text{CH}_2\text{I} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$	·0090
Trichlorolactic	$\text{CCl}_3 \cdot \text{CHOH} \cdot \text{CO}_2\text{H}$	·465
Trichlorobutyric	$\text{CH}_3 \cdot \text{CHCl} \cdot \text{CCl}_2 \cdot \text{CO}_2\text{H}$	10·0
Nitrocaproic	$\text{CH}_3 \cdot \text{CH}(\text{NO}_2) \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CO}_2\text{H}$	·0123
Dinitrocaproic	$\text{CH}_3 \cdot \text{C}(\text{NO}_2)_2 \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CO}_2\text{H}$	·0694

The constant for  $\alpha$ -iodopropionic acid is unknown, but it may be estimated as approximately equal to ·12;  $\beta$ -iodopropionic acid has thus a constant some thirteen times smaller. The great influence of position appears the more clearly as the substituent is stronger.

In the case of trichlorolactic acid the difference is still more marked. The constant of lactic acid is ·0138, and the three chlorine atoms have increased this in the ratio of 34 to 1. The same substitution for acetic acid gives an increase in no less a ratio than 67000 : 1, *i.e.* the influence in the latter case is some 2000 times greater.

Mononitrocaproic acid with the constant ·0123 conducts 8·5 times better than caproic acid. It cannot therefore be an  $\alpha$ -compound; for the nitro group proves itself to be far more negative than chlorine, and chlorine in the  $\alpha$ -position effects an eighty-fold multiplication of the constant. The number, however, corresponds very well with the supposition that the nitro group is in the  $\beta$ -position, an assumption already made from the chemical behaviour of the substance. The introduction of a second nitro group occasions an increase of the constant of mononitrocaproic acid in the proportion of 5·6 to 1. The factor for the second group is smaller than for the first, a fact in agreement with what we formerly found.

The influence of position can be investigated much more extensively for the derivatives of benzoic acid than is the case with acids of the fatty series. For example the following constants have been observed :—

Acid.		K.
Benzoic	$C_6H_5CO_2H$	·0060
o-Oxybenzoic	$C_6H_4(OH)CO_2H$	·102
m-Oxybenzoic		·0087
p-Oxybenzoic		·00286

Benzoic acid itself is more powerful than the higher fatty acids, stronger even than acetic acid. Phenyl is in general more negative than methyl, for phenyl alcohol or phenol has the characteristics of a weak acid, which is not the case with methyl alcohol. The substituting hydroxyl according as it occupies the ortho, meta, or para position is extremely different in its action. In the o-position its influence is greatest—the constant is multiplied by 17. The increase is only in the ratio 1·4:1 when it occupies the m-position, while in the p-position its entrance effects a weakening of the acid, the constant sinking to about half its former value.

This last result is especially remarkable and of great importance to every future theory of chemical affinity. For we see that here the very sign of the influence exerted by a substituting radical can vary with its position, and must thence conclude that the actions here at work are not merely greater or less according to the distance of the active substance, but depend also on the direction in which they are effective. By adding one mass to any part of another we can only increase the attraction on an external point. The increase may vary in magnitude according to the place of the new mass, but can never pass into a diminution. From the value obtained for p-oxybenzoic acid we must draw the conclusion that the action of the substituents on the affinity of acids is not of such a character as the attraction of masses; the actions must rather be represented as directed magnitudes, like velocities or forces, which have the property that their sum may be less than either of the components; the sum of two equal and opposite velocities being zero, for example.

From the effects produced by the introduction of hydroxyl into the three different positions in benzoic acid, we can very closely estimate the constants of the other oxygenated benzoic acids. The following numbers have been obtained for these substances, the position of the hydroxyls with reference to the carboxyl group being indicated by the numbers affixed to the formula, counting from the carboxyl groups as 1:—

Acid.		K.
Oxysalicylic	$C_6H_3(OH)_2CO_2H$ (2,3)	·114
Oxysalicylic	$C_6H_3(OH)_2CO_2H$ (2,5)	·108
$\alpha$ -Resoreylic	$C_6H_3(OH)_2CO_2H$ (2,4)	·052
$\beta$ -Resoreylic	$C_6H_3(OH)_2CO_2H$ (2,6)	5·0
Protocatechuic	$C_6H_3(OH)_2CO_2H$ (3,4)	·0033
s-Dioxybenzoic	$C_6H_3(OH)_2CO_2H$ (3,5)	·0091
Gallic	$C_6H_2(OH)_3CO_2H$ (3,4,5)	·0040
Pyrogallol-carboxylic	$C_6H_2(OH)_3CO_2H$ (2,3,4)	·055
Phloroglucin-carboxylic	$C_6H_2(OH)_3CO_2H$ (2,4,6)	2·2

According to what we have as yet met with, the simultaneous action of several substituents was mostly of such a character that each contributed a factor to the constant according to its nature and position. The factor was to some extent, but not entirely, independent of what already existed within the molecule, being less for the second substitution for the same group than for the first.

Thus we should be led to expect that 2, 3-oxysalicylic acid should be somewhat stronger than salicylic acid; because the m-hydroxyl, which has entered, increases the constant slightly (p. 379). Salicylic acid has the constant  $\cdot 102$ , oxysalicylic acid  $\cdot 114$ , thus confirming our expectation.

In 2, 5-oxysalicylic acid the hydroxyl likewise occupies the m-position; the two isomeric acids have therefore both the hydroxyl groups equally distant from the carboxyl. Nevertheless they are somewhat different; the 2, 5-acid being indeed stronger than salicylic acid but not so much so as the 2, 3-acid. This proves that the action of the separate substituents is to a small but still noticeable extent dependent on the others.

If the two formulæ are written down in the ordinary way with the benzene nucleus represented by Kekulé's hexagon, it will be seen that the position 2, 3 is more favourable to the mutual action than the position 2, 5.

$\alpha$ -Resorecylic acid (2,4) is produced from salicylic acid by the introduction of hydroxyl into the p-position; it should therefore be only half as powerful as the latter. Its constant  $\cdot 052$  is, in fact, only half that of salicylic acid,  $\cdot 102$ .

In  $\beta$ -resorecylic acid there are two hydroxyls in the o-position. The first hydroxyl introduces the factor 17, the second hydroxyl supplies the factor 49. This is contrary to what we found before (p. 375), viz. that the second of two like substituents effected a smaller increase than the first. The new phenomenon, however, is not a singular instance, as may be seen from the following figures:— •

Acid.		K.
Gallic . . . . .	$C_6H_2(OH)_3CO_2H$	$\cdot 0040$
Monobromogallic . . . . .	$C_6HBr(OH)_3CO_2H$	$\cdot 059$
Dibromogallic . . . . .	$C_6Br_2(OH)_3CO_2H$	$1\cdot 21$

Since the three hydroxyls occupy the places 3, 4, 5 the bromine atoms must both be in the o-position. The first bromine atom increases the constant 15 times, the second atom 20 times. Here also then the second substituent acts more powerfully than the first. From this it follows that the o-position in the benzene nucleus conditions quite different actions from the  $\alpha$ -position in fatty chains. A comprehensible geometrical explanation of these peculiar relations is not far to seek, but we cannot enter upon it here.

Protocatechuic acid with one hydroxyl in the m-position and the

other in the *p*-position, should owing to the latter be only half as strong as *m*-oxybenzoic acid. This also is actually found to be the case.

Symmetrical dioxybenzoic acid has two *m*-hydroxyls and consequently a constant ·0091, exceeding slightly that of *m*-oxybenzoic acid, ·0087. All the dihydroxylised benzoic acids thus obey the law that the constants of affinity of multisubstituted acids appear approximately as products of the factors due to each of the substituents separately.

It is also possible to calculate to a considerable degree of approximation the constants for the trioxybenzoic acids as yet known. Thus gallic acid is the *p*-oxyderivative of symmetrical dioxybenzoic acid; its constant should therefore be about half that of the latter. The actual numbers are ·0040 and ·0091. Pyrogallol-carboxylic acid, is the *p*-oxyderivative of oxysalicylic acid; the constants are ·055 and ·114—again in the ratio of 1:2. Phloroglucin-carboxylic acid, lastly, is the *p*-oxyderivative of  $\beta$ -resorecylic acid, and their respective constants are, according to expectation, 2·2 and 5·0. These relations hold good with such certainty that the constants for the three unknown trioxybenzoic acids can be given beforehand, so that once the acids are prepared, a simple measurement of their electric conductivity will suffice to determine their constitution. Other substituents in benzoic acid behave quite similarly to hydroxyl. Only a small number of the possible compounds have hitherto been measured.

Acid.		K.
<i>o</i> -Chlorobenzoic	} . . . $C_6H_4Cl.CO_2H$	·132
<i>m</i> -Chlorobenzoic		·0155
<i>p</i> -Chlorobenzoic		·0093
<i>o</i> -Bromobenzoic	} . . . $C_6H_4Br.CO_2H$	·145
<i>m</i> -Bromobenzoic		·0137
<i>m</i> -Fluorobenzoic		·0136
<i>m</i> -Cyanobenzoic	. . . $C_6H_4(CN)CO_2H$	·0199
<i>o</i> -Nitrobenzoic	} . . . $C_6H_4(NO_2)CO_2H$	·616
<i>m</i> -Nitrobenzoic		·0345
<i>p</i> -Nitrobenzoic		·0396
<i>o</i> -Nitrosalicylic	} . . . $C_6H_3(OH)(NO_2)CO_2H$	1·57
<i>p</i> -Nitrosalicylic		·89
Bromonitrobenzoic	. . . $C_6H_3Br(NO_2)CO_2H$	1·4

These numbers again call for a few remarks. Chlorine as a substituent in benzoic acid acts quite differently from hydroxyl. Whereas salicylic acid is much stronger than *o*-chlorobenzoic acid, *m*-chlorobenzoic and *p*-chlorobenzoic acids are more powerful than the corresponding hydroxyl acids. Chlorine in all three positions increases the constant. Bromine behaves very similarly to chlorine, only, while the ortho compound is somewhat stronger, the meta compound is distinctly weaker than with chlorine. *m*-Fluorobenzoic acid has exactly the



same constant as the corresponding bromine compound—an unexpected result, as hydrofluoric acid is much weaker than hydrobromic acid. Cyanogen shows its strong negative character in this case also, its influence surpassing that of chlorine; as cyanacetic acid is considerably stronger than chloracetic acid, so is *m*-cyanobenzoic acid superior in point of strength to the chlorine compound corresponding.

A group still more negative than cyanogen is the radical  $\text{NO}_2$ . In the ortho compound the constant of benzoic acid is increased one hundredfold, the constant of the meta acid is 5.7 times, and of the para acid 6.6 times greater than that of the unsubstituted compound. Here the *p*-nitrobenzoic acid appears stronger than *m*-nitrobenzoic acid, the opposite being usually the case. This circumstance renders it probable that the complex of six carbon atoms composing the benzene nucleus is not a rigid aggregate, but is rather deformable according to the nature of the atoms or radicals bound to it.

The two nitrosalicylic acids contain the nitro group in the meta position with respect to the carboxyl. They are both considerably stronger than the parent substance, and the factor in both cases is greater than that connecting benzoic and *m*-nitrobenzoic acid. Similar phenomena have already been noticed (p. 380).

Bromonitrobenzoic acid, finally, contains nitroxyl in the ortho, and bromine in the meta position. This latter, if we take the numbers for benzoic and *m*-bromobenzoic acid as basis, would more than double the constant. Thus, since *o*-nitrobenzoic acid has a constant of .62, we should expect for bromonitrobenzoic acid a number lying between 1.3 and 1.4; and this is the result of actual measurement.

Up till now we have considered almost exclusively compounds containing negative substituents, *i.e.* such as heighten the acid character of a substance. We meet with the group methyl, however, which (p. 375) under certain circumstances (*e.g.* in the passage from formic to acetic acid) diminished the value of the constant. But this is not always the case. When methyl is substituted for hydroxyl-hydrogen in glycollic acid the constant becomes greater. Ethyl acts less powerfully than methyl.

Acid.		K.
Glycollic . . . .	$\text{CH}_2\text{OH} \cdot \text{CO}_2\text{H}$	.0152
Methylglycollic . . . .	$\text{CH}_2\text{O}(\text{CH}_3) \cdot \text{CO}_2\text{H}$	.0335
Ethylglycollic . . . .	$\text{CH}_2\text{O}(\text{C}_2\text{H}_5) \cdot \text{CO}_2\text{H}$	.0234

Phenyl has already been recognised as having a greater acid-forming capacity than methyl, so we cannot be surprised that phenylglycollic acid is much stronger than glycollic acid itself.

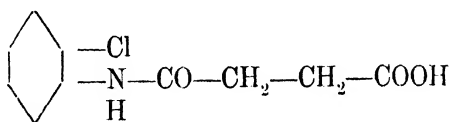
Acid.		K.
Phenylglycollic . . . .	$\text{CH}_2\text{O}(\text{C}_6\text{H}_5) \cdot \text{CO}_2\text{H}$	.0796
<i>p</i> -Nitrophenylglycollic . . . .	$\text{CH}_2\text{O}(\text{C}_6\text{H}_4 \cdot \text{NO}_2)\text{CO}_2\text{H}$	.158
<i>o</i> -Nitrophenylglycollic . . . .	$\text{CH}_2\text{O}(\text{C}_6\text{H}_4 \cdot \text{NO}_2)\text{CO}_2\text{H}$	.153

The behaviour of the two nitroderivatives of phenylglycollic acid is very remarkable. While the entrance of the nitro group into the ortho position in benzoic acid occasions a multiplication of the constant by 100, and into the para position by 6·6, in the present case it only doubles the constant. This illustrates very clearly the decreasing influence exercised by the substituent as the distance from the carboxyl group becomes greater. It will be seen also that the difference between the ortho and para positions has here almost vanished.

These relations are still more clearly apparent in the case of the following derivatives of succinic acid—

Acid.		K.
Succinanic	$\text{C}_2\text{H}_4(\text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5)\text{CO}_2\text{H}$	·00203
o-Chlorosuccinanic	$\text{C}_2\text{H}_4(\text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Cl})\text{CO}_2\text{H}$	·00208
m-Chlorosuccinanic		·00209
p-Chlorosuccinanic		·00209
o-Succinotoluidic		·00208
p-Succinotoluidic	$\text{C}_2\text{H}_4(\text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3)\text{CO}_2\text{H}$	·00193

The constants of the substituted succinanic acids are equal within the limits of the experimental error to those of the parent substance. The distance between the substituents and the carboxyl, represented in the following formula—



is consequently already greater than the distance at which the “molecular forces” are active.

Amidogen,  $\text{NH}_2$ , is of distinctly “electropositive” character, *i.e.* it weakens the acid properties of substances into which it enters. For instance, its introduction into benzoic acid gives the following numbers :—

Acid.		K.
Benzoic	$\text{C}_6\text{H}_5 \cdot \text{CO}_2\text{H}$	·0060
o-Amidobenzoic	$\text{C}_6\text{H}_4(\text{NH}_2)\text{CO}_2\text{H}$	·0009
p-Amidobenzoic		·0010
m-Amidobenzoic		·008

(approx.)

The constants of the amido acids cannot be determined with precision owing to experimental difficulties. Those for the ortho and para compounds are less than the constant of benzoic acid; but, strange to say, the constant of the meta compound exceeds it.

If an acetyl group is introduced into the amidogen, the basic properties of the latter are not only balanced, but outbalanced; the constants of the ortho and para acetamidobenzoic acids are greater than that of benzoic acid. In the para compound the weakly negative

radical effects a diminution, exactly as we found to be the case with hydroxyl (p. 379).

Acid.		K.
Benzoic	$\text{C}_6\text{H}_5 \cdot \text{COOH}$	·0060
o-Acetamidobenzoic	$\text{C}_6\text{H}_4(\text{NH} \cdot \text{CO} \cdot \text{CH}_3)\text{COOH}$	·0236
m-Acetamidobenzoic		·0085
p-Acetamidobenzoic		·0052

The foregoing examples will suffice to show the character of the information derived from the measurement of the constant of electrolytic dissociation,  $K$ ; a complete enumeration of the results already obtained in this direction would here be out of place. We shall therefore confine ourselves to some consideration of the significance and import of the constants discussed in the preceding pages.

The constants show themselves dependent on the nature and composition, and also in the highest measure on the constitution, of the substances investigated. For the dioxybenzoic acids, all having the same composition, the numbers lie between ·003 and 5·0—in the ratio of 1:1600. We have, therefore, here to deal with a property of eminently constitutive character. Now we are already acquainted with a number of constitutive properties, such as the boiling and melting points, colour, crystalline form, and the like, yet none of these allows of any definite insight into the determining cause, the chemical constitution. It is true that when the constitution has been more or less approximately ascertained by purely chemical methods, empirical relations may be found; but these remain quite on the surface and are wanting in generality. The cause of this is the insufficient character of our conception regarding the nature and extent of the influence exerted by the distribution of the atoms within the molecule on the properties in question.

I believe I am right in saying that the constant of affinity, which is of so essentially constitutive a nature, is to be put far before the other properties named above in respect of its theoretical applicability. Even now, when the constants are for the first time determined and compared, far-reaching and general conclusions can be drawn from them. The result that one and the same atom according to its "position" in the molecule exercises perfectly different actions, which are greater the more direct the relation of the atom to the carboxylic hydrogen atom, leads us to the general conclusion that these actions are functions of the distance between the atoms. In this we have for the first time a means of measuring distances in the molecule. Of course it cannot for a moment be doubted that much and arduous work has still to be done before such measurements will lead to results that will give us on all sides a complete picture of the form of the molecules; but that this object may be attained seems even already to be beyond question.

It has been stated above that the constant of affinity of acids is in general to be represented as a product, whose factors are determined by the nature and position of the elementary atoms composing the acid. This follows from the fact that analogous changes in analogous substances alter the constants in the same ratio. These factors, however, are never exactly equal, the cause of this being, of course, that no two analogous changes are exactly the same. For example, in the transformation of acetic acid into glycollic, and of propionic acid into lactic, the two changes effected are indeed very similar; but in the first case the hydroxyl has two hydrogen atoms for its neighbours, in the second case one hydrogen atom and a methyl group; it will, therefore, itself be under different influences and thus act differently on the carboxyl. The same holds true for all other corresponding cases. The approximate character of the general relation is consequently shown to be necessary; the divergence from the general scheme is conditioned by the nature of the case and will assist us in bringing the cause—the secondary actions—to light of day. What may be said universally of constitutive properties—that they can never be completely represented by any scheme, for that is essentially opposed to their nature—is particularly true for the constants of affinity. The multiplicity of nature is specially manifest in them, producing within a framework of the broadest generalities the most delicate individualisation.

The form of the constants of dissociation as a product of factors,  $k = k_1 k_2 k_3 \dots$ , has a deeper meaning, to be seen by reverting to the formula of dissociation itself. This was obtained from thermodynamics in the following form (p. 314)

$$\lg \frac{p}{p_1 p_2} = \frac{\rho}{RT} + C,$$

where  $p_1$  and  $p_2$  are the partial pressures of the products of decomposition,  $p$  that of the undecomposed substance,  $\rho$  the heat of dissociation,  $T$  the absolute temperature,  $R$  the gas-constant, and  $C$  a value which is only a function of the temperature,—which, therefore, at a steady temperature may be regarded as a constant.

In the case before us  $p_1 = p_2$ , and as  $p_1$  and  $p$  are proportional to  $\frac{m}{v}$  and  $\frac{1-m}{v}$ , it follows that  $\frac{p_1}{p_2} = \frac{(1-m)v}{m^2}$ , and consequently

$$\lg \frac{(1-m)v}{m^2} = \frac{\rho}{RT} + C$$

or

$$\lg \frac{m^2}{(1-m)v} = -\frac{\rho}{RT} + C'.$$

Now the constant of affinity  $k = \frac{m^2}{(1-m)v}$ ; and as in general  $k =$

$k_1 k_2 k_3 \dots$ , we have

$$\lg k_1 + \lg k_2 + \lg k_3 + \dots = -\frac{\rho}{RT} + C'.$$

The constant  $C'$  depends only on the units and points of origin chosen; therefore, if on the left-hand side there appears a sum of terms  $\lg k$ , to each of these on the right-hand side there must correspond a term  $-\frac{\rho_n}{RT}$  so that  $\frac{\rho}{RT}$  is likewise resolved into a sum of terms,

$$-\frac{1}{RT}(\rho_1 + \rho_2 + \rho_3 + \dots), \quad k_n \text{ always corresponding to } \rho_n.$$

In other words: The natural logarithm of the constant of affinity (or dissociation) is proportional to the heat of dissociation of the acid on its decomposition into ions. As the former is composed of a series of terms depending on the nature and position of the constituent atoms, the heat of electrolytic dissociation must be determined by a corresponding number of terms each depending on the nature and position of one of the atoms.

Now in this case the heat of dissociation is an exact measure of the work done on the separation of the replaceable hydrogen atom from the negative ion, since there is no external work and the state of the substances under consideration approaches the ideal gaseous state. Consequently the heat of dissociation measures the potential function of the atomic complex for the corresponding state, and we see that this potential is the sum of those values which the separate atoms contribute to the total according to their nature and position. Elements like chlorine, sulphur, etc., which increase the constant  $k$ , diminish the heat of dissociation; for  $\lg k$  and  $\rho$  have opposite signs. Amidogen, on the other hand, which diminishes the constants increases the heat of dissociation, *i.e.* increases the work necessary for separating the replaceable hydrogen atom.

In these considerations the question already discussed—the connection between chemical affinity and heat of reaction, finds its theoretical explanation.

Here too we see the essentially constitutive constants of affinity resolved into the additive form. This was done by the influence of constitution, or relative position, being itself included in the terms to be summed. A similar development awaits the theory of all constitutive properties; for no other form to express the common action of different elements seems imaginable to us than the form of a sum.

